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Editor's Page

The shortness of time . . .

As I get older, time seems to get shorter. Although many experience this feeling, the duration of time is not changing, only our perception of it. However, in the five decades I have been involved in science, the timescale at which we are able to measure phenomena has shortened by nine orders of magnitude.

When I was in college and graduate school, nanosecond (10^{-9} s) laser pulses were used to study molecular dynamics. For example, you could measure how long it took, after absorbing a photon, before a molecular bond was broken and the parts flew away from each other. Towards the end of my academic career, the duration of laser pulses had shortened to picoseconds (10^{-12} s) and femtoseconds (10^{-15} s). It was in 1999 that Ahmed Zewail from the California Institute of Technology received the Nobel Prize in Chemistry for his studies of the transition states of chemical reactions using femtosecond laser spectroscopy.

The 2023 Nobel Prize in Physics announced last month was about time, and the fact that the measurement timescale in physics and chemistry really is getting shorter over the years, and is now at the attosecond scale (10^{-18} s). It was for their ability to generate and measure attosecond laser pulses that the three winners — Anne L'Huillier, professor at Lund University; Ferenc Krausz, director at the Max Planck Institute of Quantum Optics and professor at Ludwig-Maximilians-Universität Munich; and Pierre Agostini, professor at The Ohio State University — were awarded the 2023 Physics Prize. With attoseconds, it is now possible to monitor the dynamics of the electrons within atoms or molecules.

One cannot predict the impact such research will have on the chemical process industries (CPI). For sure, the ability to study the motion of electrons is of interest today, with the growing importance of electrochemistry and materials science. The more we understand — at the fundamental level — how matter interacts with light and how electrons move in and out of molecules, the better will our chances be of developing the next generation of solar cells, electrolyzers and electronic devices. One only needs to look at the advancements in sensor technology and the role lasers play in gas detectors to see today's "fruits" of yesterday's basic research. The addition of attosecond spectroscopy to our analytical toolbox will certainly find its practical applications — it is only a matter of time.

. . . and space

As the measurement timescale has shrunk, so has the size of the particles in chemical powders. The 2023 Nobel Prize in Chemistry was awarded for the discovery and synthesis of quantum dots — nanoparticles that are so small that their size determines their physical properties, which are governed by quantum mechanical effects. The winners for the prize are Moungi Bawendi, professor at the Massachusetts Institute of Technology; Louis Brus, professor at Columbia University; and Alexei Ekimov, former chief scientist at Nanocrystals Technology, Inc. Their pioneering work over the last 20–30 years is already bearing fruit, with many commercial applications of quantum dots already realized, such as in computer and television screens, in some light-emitting diodes for illumination, and in biomedical applications for mapping cells and organs. A lot of research is underway to further develop other applications, such as in photocatalysis. (For more on quantum dots, see *Chem. Eng.*, April 2019, pp. 14–17). ■

Gerald Ondrey, Senior Editor

Chementator

Using waste plastic to simultaneously make graphene and hydrogen

Building off of a process to efficiently manufacture graphene (see *Chem. Eng.*, April 2022, p. 9), a team of researchers from Rice University (Houston, www.rice.edu) have uncovered that the process can be easily altered to also produce a nearly pure stream of hydrogen gas using mixed-waste plastic materials as the feedstock. The previous work focused making flash graphene using any carbon source, including petroleum coke, coal, food waste or biochar, but now the team is looking to waste plastics, such as polypropylene and polyethylene, due to their higher hydrogen content. "We noticed gas coming out of the reaction as it heats to over 3,000K in the first 3 ms. We were only trapping a small amount of this gas," explains James Tour, professor of materials science and nanoengineering at Rice. Upon analysis, the team found that the gas was 92–94% H_2. By swapping coke feedstock for waste plastics, which have a more favorable weight percentage of hydrogen (around 14 wt.%) and a very low cost, the process can maximize hydrogen production while also producing graphene at a high yield.

"We take the plastic and put a high-current voltage through it and add a small amount of carbon additive, such as metallurgical coke, to increase the conductivity of the plastic, and it forms graphene and hydrogen," explains Tour. The ability to use a low-cost feedstock, along with the purity of the H_2 produced, make the process economics very favorable, emphasizes Tour. "If we can sell the graphene at \$3,000/ton, the amount of H_2 that comes out will essentially cost negative \$4.30/ton."

The next steps will be to find a partner to license and scale up the plastics-based technology. Universal Matter (Houston; www.universalmatter.com) is set to start up a demonstration plant for rapid flash-Joule heating in the coming months, producing 1 ton/d of graphene from metallurgical coke feedstock.

The first H_2-fired low-NOx burner for traveling-grate pelletizing plants

Last month, Metso Corp. (Espoo, Finland; www.mogroup.com) introduced a hydrogen-variant of its Ferroflame LowNOx burners as part of its NextGen Pelletizing plant product range. It is a first-of-its-kind burner to run on H_2 and to operate on the LowNOx combustion principle. Designed especially for traveling-grate pelletizing plants, these burners are 100% H_2 powered and are part of Metso's Planet Positive offering, which focuses on environmentally efficient technologies.

H_2-powered Ferroflame LowNOx burners use the same combustion principle as that of Ferroflame LowNOx burners for natural gas launched in 2022 (*Chem. Eng.*, May 2022, p. 8). They can replace traditional burners in a traveling-grate pelletizing plant, and the Ferroflame LowNOx burners for natural gas can be modified to run on H_2.

"We are very excited to bring the hydrogen-variant of the Ferroflame LowNOx burner for traveling-grate pelletizing plants to the market," says Andreas Munko, senior product manager, Ferrous and Heat Transfer at Metso. "Its laboratory-proven functionality and performance with hydrogen can be implemented in pelletizing plants and can help customers in meeting CO_2 and NOx targets. We see these burners as a stepping-stone towards decarbonization of the pelletizing industry," he says.

The H_2 burners are part of Metso's NextGen Pelletizing concept, which is designed on the vision for the next generation of pelletizing plants that strive to be carbon-neutral and autonomous. Metso also has a suite of digital solutions that help improve process performance, production capacity and product quality, as well as reduce energy consumption, environmental impact and operation and maintenance costs.

BIO-ACRYLONITRILE

Site selection is underway for a glycerol-to-acrylonitrile demonstration-scale plant that will enable the production of plant-based acrylonitrile (ACN). Trillium (Knoxville, Tenn.; www.trilliumchemicals.com) is partnering with Zeton (Oakville, Ont.; www.zeton.com) to design and build the plant, known as Project Falcon. The demonstration facility is being scaled up from a pilot plant that has been operating since 2022 (*Chem. Eng.*, April 2022, p. 8). Using a two-step process whereby glycerol is dehydrated to acrolein, which then undergoes an ammoxidation reaction to produce ACN, the Trillium demonstration plant will produce ACN for a number of applications, including acrylonitrile, butadiene, styrene (ABS) plastic, rubber, acrylic fabrics, carbon fibers and others. The facility will focus on de-risking the technology, while also producing sufficient material for sample testing by partners, such as Solvay and HyoSung, explains Trillium independent board chair Erik Scher. Trillium is currently evaluating four sites, and depending on the particulars of the site selected for the plant, it is likely to begin operation sometime in 2025.

LARGE-SCALE MOF PRODUCTION

BASF SE (Ludwigshafen, Germany; www.basf.com) is said to be the first company to produce metal-organic frameworks (MOFs) on a production scale of several hundred tons per year. A first project has now been successfully completed for Svante Technologies Inc. (Burnaby, B.C., Canada; svante.com). The interdisciplinary BASF team of researchers, scaleup experts and engineers worked collaboratively on the scaleup by converting the Svante laboratory recipe into a safe plant procedure for large-scale production. The MOFs produced will be used as solid sorbents for carbon-capture projects.

MOFs are highly crystalline structures with nanometer-sized pores and a large surface area. This structure offers a high capacity for the storage of CO_2, the dehumidification of air for room climate control and the adsorption of the greenhouse gas methane. BASF has developed expertise on the scaleup and production of MOFs, can tailor MOFs to application requirements and specifications, and today has the capacity to produce customized MOFs for various applications and industries.

TAR-FREE SYNGAS

Although biomass gasification has been around for centuries, the synthesis gas (syngas) produced contains numerous hydrocarbons, also called tars, which are detrimental to process equipment and can be hazardous to human health. Although research has

Precise degradation control is key to advanced bioresorbable polymers

Bioresorbable polymers — those that degrade naturally over time and can be absorbed by the body — are essential for delivering a number of advanced biomedical technologies to patients, including long-acting injectable or implanted products, regenerative scaffolds, degradable medical devices, dermal fillers and drug products with highly sensitive ingredients, such as mRNA. Ashland Inc. (Wilmington, Del.; www.ashland.com) has developed proprietary production and purification processes for a new line of bioresorbable polymers (photo), Viatel ultrapure (poly-D,L-lactide-co-glycolide/poly-D,L-lactide). This scalable process enables a more neutral pH environment during production when compared to traditional Viatel grades, which significantly decreases the amount of residual acidic monomers and overall acidity over time, a significant benefit for the production of acid-sensitive drug ingredients. The removal of residual monomers results in a more consistent rate of water uptake and improved degradation kinetics. Furthermore, the neutralized production environment means that polymer-degradation behavior — crucial to the performance of bioresorbable products — is more consistent and controllable.

According to Ashland, the higher purity achieved by the new Viatel ultrapure process, when compared to other bioresorbable products, leads to a prolonged structural integrity, meaning that products formulated with the materials exhibit more consistent drug-release profiles as the polymer breaks down. "This means that chemists can predict or program the chemistry to degrade and break down over a set period of time. This set of properties allows formulators to take their drug molecule, incorporate it within a polymer depot, deliver that depot into the patient and then allow the depot to slowly break down over time. The advantage is that you can sustain release over several weeks or months, based on the programmable polymer chemistry that Ashland provides," says Sean McMahon, business development manager at Ashland. A particular area where this type of tunability is especially advantageous is in treating tumors, because the treatment must be potent enough to destroy or disrupt the tumor site, but precisely targeted so that it does not cause adverse effects to nearby tissues. The Viatel ultrapure technology was introduced in October at the American Association of Pharmaceutical Scientists' PharmaSci 360 event in Orlando, Fla.

Ashland

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tested a wide variety of methods from filters to absorbers to exotic systems involving plasma, a practical solution to managing these tars has remained elusive.

Last month, Frontline BioEnergy LLC (Nevada, Iowa; frontlinebioenergy.com) said that it achieved a breakthrough in syngas quality for biomass gasification at its new pilot facility located in Nevada, Iowa. The company's TarFreeGas technology achieved the ultimate goal of biomass gasification: ultra-clean biomass-derived syngas.

"We were thrilled when our results began to show non-detectable levels of all tars leaving the catalytic gas converter," says T. J. Paskach, Frontline's chief technology officer.

TarFreeGas utilizes a pressurized (up to 10 bars) reactor containing a fluidized bed of sand and can operate with either air and steam or pure oxygen and steam. TarFreeGas causes tar levels up to 99% lower than traditional fluidized-bed gasifiers, the company says.

MEMBRANES

Osmoses (osmoses.com), a spinoff of the Massachusetts Institute of Technology (MIT; both Cambridge, Mass.; www.mit.edu), has raised an oversubscribed $11-million seed round led by Energy Capital Ventures. Os-

Closed-loop CO$_2$-based energy-storage system slated for Wisconsin

Alliant Energy (Madison, Wis.; www.alliantenergy.com) was recently selected to receive a $30-million grant from the U.S. Dept. of Energy's Office of Clean Energy Demonstrations (OCED; Washington, D.C.; www.energy.gov/oced) for a proposed 200-MWh energy storage system. Alliant Energy's new battery system, known as the Columbia Energy Storage Project, would be the first-of-its-kind in the U.S.

The Columbia Energy Storage Project would utilize an innovative design by Energy Dome S.p.A. (Milan, Italy; www.energydome.com) to deliver 10 h of energy-storage capacity by compressing carbon dioxide gas into a liquid. When that energy is needed, the system converts the liquid CO$_2$ back to a gas, which powers a turbine to create electricity. By storing the CO$_2$ in the liquid phase at ambient temperature, Energy Dome is able to reduce the typical storage costs associated with compressed-air energy storage, without having to deal with cryogenic temperatures associated with liquid-air energy storage, the company says. The first commercial demonstration facility of the CO$_2$ Battery — a 4-MWh system located in Sardinia, Italy — was launched in June 2022.

Development of the Columbia Energy Storage Project is being led by Alliant Energy in partnership with WEC Energy Group, Madison Gas and Electric, Shell Global Solutions U.S., the Electric Power Research Institute, the University of Wisconsin at Madison and Madison College.
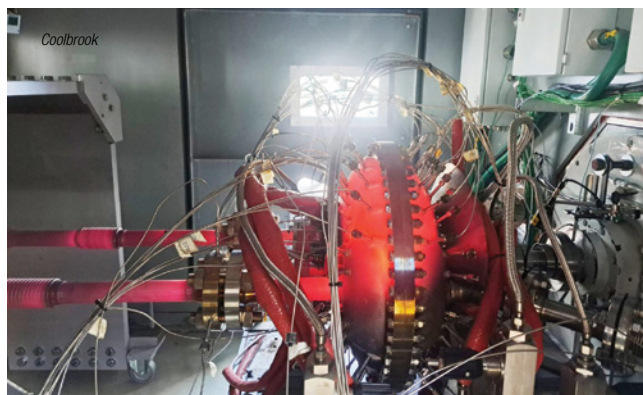
The facility will be built south of Portage, Wis. in the town of Pacific, near the current Columbia Energy Center. Alliant Energy expects to submit project plans to the Wisconsin Public Service Commission in the first half of 2024. Pending approval, project construction could begin in 2025 with completion in 2026.

First-phase pilot tests completed to demonstrate RotoDynamic technology

Coolbrook Oy (Helsinki, Finland; www.coolbrook.com) has successfully completed the first phase of large-scale pilot testing (photo) for its RotoDynamic Technology at the Brightlands Chemelot Campus in Geleen, the Netherlands. During 2023, Coolbrook has been running a test program to demonstrate the RotoDynamic Heater (RDH) technology, which combines the principles of rocket science, turbomachinery and chemical engineering to electrify and decarbonize traditionally hard-to-abate industrial processes, such as processing in cement, iron and steel and chemicals. Industrial partners include Cemex, UltraTech Cement and Arcelor Mittal.

The now completed test phase has demonstrated RDH technology's capabilities for industrial use in high-temperature process heating, enabling the technology to move forward to industrial-scale projects at customer sites. The pilot testing has reached temperatures as high as 1,000°C, which already exceeds the temperature range of conventional resistive heaters by several hundred degrees. The tests have also validated Coolbrook's technical pathway up to 1,700°C, covering more than 95% of the temperature range required to cover the €1-trillion industrial-heating market. The next test phase will encompass the demonstration of RotorDynamic Reactor (RDR) technology, which produces olefins and aims to decarbonize the petrochemical industry (for more about RDR, see *Chem. Eng.*, May 2017, p. 9). For this application, several industrial partners are involved, including Braskem, ABB, Linde Engineering, Shell and SABIC. Academic partners include the universities of Gent, Oxford and Cambridge.

Coolbrook

Commenting on the new milestone, Liping Xu (formerly Cambridge University) and Budimir Rosic of Oxford University said: "The Coolbrook proprietary RotoDynamic Technology is probably the most innovative application of turbomachinery after its application in gas turbine engines as aviation power. It is set to bring forth a fundamental and revolutionary impact on the petrochemical industry and other high-temperature industries for greenhouse gas reduction. For the first time, it is shown that by using renewably-powered RDR and RDH, it is possible to completely decarbonize the highest-emitting industries that have been labeled as 'hard-to-abate.'"

Coolbrook expects to deploy the technology in industrial-scale projects at customer sites, aimed to be operational in 2024, while full commercial deployment is expected to start around 2025.

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moses will use the funding to develop commercial-scale membrane modules for field deployment and establish pilot partnerships. The company also recently a $1.5-million grant from the U.S. Dept. of Energy, as well as additional grant support from ARPA-E and NSF, among other organizations.

Osmoses has developed a patented membrane technology that purifies gas molecules with "unprecedented" flux and selectivity — even for gases of similar size (for more details, see *Chem. Eng.,* May 2022, pp. 8–9).

BIOREACTOR DEVELOPMENT

To facilitate the configuration of bioreactors, GEA Group (Düsseldorf, Germany; www.gea.com) has developed a digital twin for virtual testing prior to construction. The aim is to create an optimum growth environment for cultured cells, which behave differently in mass production volumes than at laboratory scale.

"A digital twin simulates the environment inside bioreactors in a wide variety of scenarios. This lets us precisely

A single flow reactor produces a toxic precursor, an unstable reagent and product

The Vilsmeier reagent (VR), $[(CH_3)_2NCHCl]Cl$, is necessary for producing a large range of pharmaceuticals, but it is unstable in air and is made from the toxic precursor phosgene ($COCl_2$). A new flow-reactor system has been developed by Akihiko Tsuda, associate professor in the Chemistry Department of Kobe University (Japan; www.kobe-u.ac.jp) that safely produces everything — precursor, reagent and product — on-site and on-demand.

In earlier work, Tsuda's research group demonstrated the production of phosgene on-demand by the photochemical oxidation of chloroform using ultraviolet (UV) radiation in a batch vessel. Now, the researchers have converted the batch process into a continuous one, which makes it possible for performing phosgene-based reactions, including the generation of, and synthesis with, the Vilsmeier reagent.

In a recent issue of *Organic Process Research & Development*, the researchers report the flow synthesis of acyl chlorides and VR with phosgene. This system is said to be applicable to the continuous-flow synthesis of esters, carboxylic anhydrides, amides, aryl aldehyde precursors and β-chloroacrolein precursors.

"This reaction system consumes less energy, produces less waste, and enables versatile, as well as scalable, chemical synthesis," says Tsuda. "These features contribute positively to the lifecycle assessment of the products, which is especially important in the industry."

The research was supported by the Adaptable and Seamless Technology Transfer Program through Target-driven R&D (ASTEP), Seeds development type from the Japan Science and Technology Agency (JST).

A new heat-resistant membrane

Most polymeric membranes degrade during use, making them impractical for industrial separation processes. To solve this problem, researchers from the State University of New York at Buffalo (SUNY Buffalo; www.buffalo.com), with cooperation for scientists at Rensselar Polytechnic Institute, have created a new, sturdier membrane that can withstand harsh environments — high temperatures, high pressure and complex chemical solvents — associated with industrial separation processes. Made from a carbon-doped metal oxide, it is described in a recent issue of *Science*.

"The processes of separating molecules — whether for water desalination, the production of medicine or fertilizers — use an incredible amount of energy," says the study's corresponding author, Miao Yu, SUNY Empire Innovation Professor in the Deptartment of Chemical and Biological Engineering in the University at Buffalo School of Engineering and Applied Sciences. "What we have developed is a technique to easily fabricate defect-free, strong membranes that have rigid nanopores that can be precisely controlled to allow different-sized molecules to pass through."

The researchers combined chemical vapor deposition and interfacial polymerization to create the membrane. In experiments, researchers merged two low-cost reactants — liquid ethylene glycol and gaseous titanium tetrachloride — on a ceramic support. Within minutes, the reaction created a thin film. The film is then sintered to burn off carbon, which create nanopores with a diameter of 0.6 to 1.2 nm, depending on the gas environment and the heating time. For a given pore size, these nanofilms have 2 to 10 times higher pore density (assuming the same tortuosity) than reported for commercial organic solvent nanofiltration membranes, yielding ultra-high solvent permeance, even if they are thicker, the researchers report. The new membrane can withstand temperatures up to 284°F and pressures up to 30 atm when exposed to organic solvents.

To demonstrate the membrane's effectiveness, the team showed it could separate the fungicide boscalid from its catalyst and starting reagent. The entire process occurred at 194°F.

Ultrathin films achieve record hydrogen separation

Scientists at École Polytechnique Fédérale de Lausanne (EPFL; Switzerland; www.epfl.ch) have synthesized the first ever metal-organic frameworks (MOFs) membrane with the thickness of just one unit cell. The ultrathin film yields record-high performance for the separation of hydrogen from nitrogen.

The research team, led by professor Kumar Varoon Agrawal at EPFL's School of Basic Sciences, worked with a type of MOFs known as zeolitic imidazolate frameworks (ZIFs). To make the films, the researchers used a crystallization method that capitalizes on the precise alignment of ultra-dilute precursor mixtures with the underlying crystalline substrate. By carefully controlling precursor concentrations and interactions with the substrate, the team was able to suppress out-of-plane growth — a common problem in making thin films.

Within a matter of minutes, and at room temperature, the scientists were able to fabricate macroscopically uniform two-dimensional ZIF films with a thickness of only one unit cell, measuring only 2 nm. The scientists also showed that the process is scalable, preparing films with area of hundreds of square centimeters. The breakthrough overcomes conventional methods, which have limited ZIF film thickness to 50 nm.

The ZIF film has a unique configuration: a nanometer-thick film with a uniform array of hydrogen-sieving, six-membered, zinc-imidazolate coordination ring. "This allows for an exceptional combination of hydrogen flux and selectivity, holding immense potential for highly efficient gas-separation applications," Agrawal explains.

The development was described in a recent issue of *Nature Materials*, with contributions from scientists at Johns Hopkins University, King Abdullah University of Science and Technology and Soochow University. ∎

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match the tank design and the mechanical configuration for fine-tuning parameters, such as shear stress, temperature, nutrient and oxygen distribution, to what the cells need," explains Daniel Grenov, product manager Bioreactor Technologies at GEA. The virtual bioreactor testing is based on computational fluid dynamics (CFD), which models the growth behavior of cells, as well as the oxygen and nutrient delivery radii inside the reactor. "Experts estimate that, when scaling up bioreactors, uneven distribution of oxygen and nutrients inside the tank often leads to performance losses of up to 30%," Grenov says.

By using CFD simulation and calculating kinetic models, combined with physical test rigs to measure bubble sizes and equipment behavior, the performance of large-scale bioreactors can be optimized before they are fabricated.

HIGH-TEMPERATURE HEAT PUMP

At this year's *Wirtschaftsnacht Rheinland*, SPH Sustainable Process Heat GmbH (Overath, Germany; www.spheat.de) won the award in the "Start-up" category. The company produces an innovative and extremely efficient high-temperature heat pump for the industry — the ThermBooster. The core of the heat pump is a special piston compressor. In combination with environmentally friendly refrigerants and innovative process technology, the ThermBooster is one of the first industrial heat pumps in the world that can generate steam at temperatures of up to 165°C. The company is working to increase this to 200°C in the future.

Since being founded by the managing directors Andreas Mück and Tim Hamacher in 2020, the company has filed three patents and is now working on projects worldwide.

3D PRINTED FIBERS FOR IMPLANTS

Last month, Evonik Industries AG (Essen, Germany; www.evonik.com) introduced a new carbon-fiber reinforced polyether ether ketone (PEEK) filament, for use in additive manufacturing (3D printing) of medical implants. This "smart" biomaterial can be processed in common extrusion-based 3D printing technologies, such as fused-filament fabrication (FFF).

Dubbed Vestakeep iC4612 3DF and Vestakeep iC4620 3DF, the two available filaments feature 12% and 20% carbon fiber content, respectively. The two grades offer a choice of material depending on the desired strength and flex properties of 3D-printed implants, such as bone plates and other reconstructive prostheses.

Evonik's filaments provide strength from the high carbon-fiber content, matched with the ductility of its PEEK component. Additional product benefits include the ability to define the alignment of the carbon fibers during the 3D-printing process, high bio-compatibility for metal-allergy patients and no X-rays artifacts. ❐

Business News

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Plant Watch

BASF to build a new fermentation plant in Ludwigshafen

October 12, 2023 — BASF SE (Ludwigshafen, Germany; www.basf.com) is investing in a new fermentation plant for biological crop-protection products, such as fungicides, insecticides and seed treatments, at its Ludwigshafen site. Commissioning is planned for the second half of 2025.

Clariant opens new flame-retardants production facility in China

October 12, 2023 — Clariant AG (Muttenz, Switzerland; www.clariant.com) has opened its new production facility for halogen-free organophosphorus flame retardants in Daya Bay, Huizhou, China. This is the plant's first production line. A second line is under construction and expected to be onstream during 2024.

Repsol starts up 'green'-hydrogen electrolyzer at Petronor complex

October 10, 2023 — Repsol S.A. (Madrid, Spain; www.repsol.com) has begun producing renewable hydrogen at its Petronor industrial center in Biscay, Spain. The site's 2.5-MW electrolyzer can generate 350 metric tons per year (m.t./yr) of hydrogen for industrial use, mainly in the Petronor petroleum refinery. Petronor will be the site for two more electrolyzers, with capacities of 10 MW and 100 MW, in the coming years.

Petronas Chemicals to build Asia's largest advanced plastics-recycling plant

October 10, 2023 — Petronas Chemicals Group Berhad (PCG; Kuala Lumpur, Malaysia; www.petronas.com) plans to construct Asia's largest advanced plastics-recycling plant with a capacity of 33,000 m.t./yr. The plant, which will be located in Pengerang, Johor, is targeted to be operational by the first half of 2026.

BASF expands production capabilities for emollient specialty products

October 10, 2023 — BASF is investing in the production of emollient specialty products at its Düsseldorf site. A new reactor and upgrade of the distillation units enable an expansion of production capacity to meet the increasing demand. The new facilities are scheduled to go into operation in the third quarter of 2025.

Toray to expand production capacity for carbon fibers in France

October 4, 2023 — Toray Industries, Inc. (Tokyo, Japan; www.toray.com) will expand French subsidiary Toray Carbon Fibers Europe's production facilities for regular-tow medium- and high-modulus carbon fibers. This expansion will increase annual capacity at the Abidos plant in France from 5,000 m.t./yr to 6,000 m.t./yr. Production is expected to start in 2025.

TPC Group completes initial phase of diisobutylene expansion

October 2, 2023 — TPC Group (Houston; www.tpcgrp.com) has completed the initial phase of its diisobutylene (DIB) capacity upgrade to supply the growing global demand for DIB driven by the adoption of low global-warming-potential refrigerants. DIB is a raw material in the manufacture of components of the lubricants used in next-generation cooling systems.

DuPont opens new adhesives plant in China

September 28, 2023 — DuPont (Wilmington, Del.; www.dupont.com) opened its new adhesives production facility in Zhangjiagang, China. The new facility will produce adhesives to serve the transportation industry, primarily in lightweighting and vehicle electrification applications. The facility will produce a number of products, including conductive adhesives, thermal interface materials, multi-material bonding adhesives, structural adhesives and more.

Huntsman begins construction on new pilot plant for carbon nanotube materials

September 28, 2023 — Huntsman Corp. (The Woodlands, Tex.; www.huntsman.com) commenced construction on its 30-m.t./yr carbon-nanotube (CNT) materials plant. The new plant, which converts methane gas to carbon nanotubes and hydrogen, will be one of the largest of its kind in the Americas. Huntsman's CNT-based materials can be produced as sheets, tape, yarn or additives.

Arkema to expand dimethyl disulfide production capacity in Texas

September 28, 2023 — Arkema S.A. (Colombes, France; www.arkema.com) is increasing global production capacity of dimethyl disulfide (DMDS), an additive that is used in the production of renewable fuels, at its Beaumont, Tex. site. Arkema also produces DMDS in Lacq, France and Kerteh, Malaysia.

Mergers & Acquisitions

Evonik announces formation of biotech JV in China

October 12, 2023 — Evonik Industries AG (Essen, Germany; www.evonik.com) announced that Evonik China Co. and Shandong Vland Biotech Co. agreed to form a joint venture (JV) to expand their presence in animal-feed additives. Both partners will bring their relevant businesses — such as probiotics — into the JV to serve the greater China region, which accounts for more than 20% of the global feed-additives market.

Topsoe and Aramco to set up a hydrogen demonstration plant

October 11, 2023 — Topsoe A/S (Lyngby, Denmark; www.topsoe.com) and Aramco (Dhahran, Saudi Arabia; www.aramco.com) have announced a new collaboration to demonstrate technology for the production of low-carbon hydrogen. As part of the agreement, Aramco and Topsoe will build a demonstration plant at the Shaybah natural-gas liquids (NGL) recovery plant in Saudi Arabia. In the project, renewable electricity will be used for electrified steam-reforming to produce low-carbon hydrogen.

TotalEnergies and Borealis start up joint polyethylene unit in Texas

October 9, 2023 — TotalEnergies SE (Paris; www.totalenergies.com) and Borealis AG (Vienna, Austria; www.borealisgroup.com) have started up their Baystar JV's 625,000-m.t./yr Borstar polyethylene (PE) unit, which more than doubles the current production capacity at Baystar's site in Bayport, Tex. The new $1.4-billion unit completes the partners' integrated petrochemicals JV, which has over 1 million m.t./yr of total production capacity.

Lubrizol sells surfactant manufacturing plant in California

October 4, 2023 — The Lubrizol Corp. (Cleveland, Ohio; www.lubrizol.com) has divested substantially all of the assets of its Paso Robles, Calif., surfactant manufacturing facility to Coast Southwest, Inc. (Irving, Tex.). The plant makes surfactants used in a wide range of personal-care and industrial products.

Wood and OMV collaborating on plastic-recycling technology

October 4, 2023 — John Wood Group plc (Wood; Aberdeen, U.K.; www.woodplc.com) signed a collaboration agreement with OMV AG (Vienna, Austria; www.omv.com) for the commercial licensing of OMV's ReOil advanced plastic-recycling technology. Under the collaboration, Wood and OMV will bring ReOil jointly to the market, combining Wood's proprietary heater technology with OMV's chemical recycling process.

Stratasys sells urethane manufacturing plants in California

October 2, 2023 — 3D-printing solutions provider Stratasys Ltd. (Eden Prairie, Minn.; www.stratasys.com) completed the sale of the Stratasys Direct urethane facilities located in Poway, Calif. to the Lamarjean Group. Stratasys Direct is the company's on-demand parts service bureau. The decision to sell the non-core urethane facilities is part of an operational transformation effort that began in early 2023.

Eastman to sell Texas City operations to Ineos

September 28, 2023 — Eastman Chemical Co. (Kingsport, Tenn.; www.eastman.com) entered into a definitive agreement to sell its Texas City Operations to Ineos Acetyls, a manufacturer of acetic acid and related chemicals owned by Ineos Ltd. (London, U.K.; www.ineos.com). The total sale price for the assets is $490 million. Eastman will retain ownership of its plasticizer business at the site, which Ineos will operate for Eastman. ■

Mary Page Bailey

Commercial Progress on Turquoise Hydrogen

Producing hydrogen via methane pyrolysis – termed 'turquoise hydrogen' – has thus far received less attention than 'blue' and 'green' H_2, but it may offer advantages over both

While the vast majority of current hydrogen production occurs by steam reforming of methane, there is an ongoing global effort to increase production of low-carbon hydrogen (hydrogen generated with minimal or zero associated emissions of carbon dioxide). The possibilities for low-carbon H_2 include steam-methane reforming (SMR) coupled with carbon capture and storage (CCS) — known as "blue" H_2 — and direct electrolysis of water using renewable energy — so-called "green" H_2.

Another option for sustainable H_2 production without CO_2 emissions is methane pyrolysis (MP), the breakdown of CH_4 bonds in the absence of air to form H_2 and solid carbon. Known as "turquoise H_2," the set of processes being explored around methane pyrolysis have received less attention than green and blue hydrogen thus far, but the technique offers compelling benefits over the other two, including zero or minimal CO_2 emissions with lower costs than green H_2 and a potentially valuable co-product.

On p. 21 of this issue, readers can find an article on the fundamentals of the methane pyrolysis reaction and some of the main technical challenges with producing H_2 in this way. Here, the various approaches to commercializing turquoise H_2 are discussed, along with the progress to date. "There are many ways to produce H_2 by methane pyrolysis — all differing in terms of the heat-delivery mechanism, catalyst, process conditions and type of solid carbon produced," says Chingis Idrissov, technology analyst at IDTechEx (Cambridge, U.K.;

www.idtechex.com). "And now, a large number of players worldwide are developing this technology, including many startup companies and academic research groups, along with some large companies as well."

Table 1 provides brief descriptions of several company-led and academic efforts in developing turquoise H_2 processes, as found in recently surveyed literature and through contacts with technology developers. An expanded version of the table can be found in the online version of this article at www.chemengonline.com.

Commercial production

Emerging methane-pyrolysis technologies can be categorized by their approach to breaking down CH_4. Among the methods are thermal and catalytic reactors employing plasma (hot, warm and cold), molten-media bubble columns, fluidized beds, moving beds and hybrid arrangements. Other developing technologies encompass compression heating using shock waves and pulsed-flow reactors, as well as chemical decomposition employing redox reactions.

Thermal plasma-arc reactor technology has the longest history of development and is the only one being commercially implemented at present. Monolith Inc. (Lincoln, Neb.; www.monolith-corp.com), widely considered to be the leader in commercial development of turquoise H_2, purchased and further developed intellectual property from Kvaerner (now Aker Solutions) to produce H_2 using a plasma-arc approach.

Monolith currently operates the first commercial MP facility for turquoise H_2, known as Olive Creek 1

Monolith

FIGURE 1. Monolith's Olive Creek 1 facility is currently producing H_2 and carbon black in Nebraska

(OC1; Figure 1), in Hallam, Neb. The first-of-its kind commercial facility is designed to produce hydrogen and up to 14,000 metric tons of carbon black per year with virtually zero emissions from operations. Monolith will begin construction on Olive Creek 2 at the same site in 2024. The expanded facility will have 12 additional MP reactors. To allow for the expansion of clean H_2 production, along with carbon black and NH_3, Monolith received conditional approval for a $1.04 billion loan from the U.S. Department of Energy in December 2021.

OC1 has allowed the company to make significant improvements to the process prior to the planned scaleup in OC2. Monolith co-founder and CEO Rob Hanson says making the scaled up plant work reliably for commercially relevant periods of time required diligent work, but they company has made hundreds of tweaks to improve production. OC2 will add an ammonia plant that will make approximately 300,000 ton/yr of ammonia from the hydrogen generated.

Two major areas of focus at Monolith have been to develop a highly detailed understanding of the methane pyrolysis reaction, and to control the
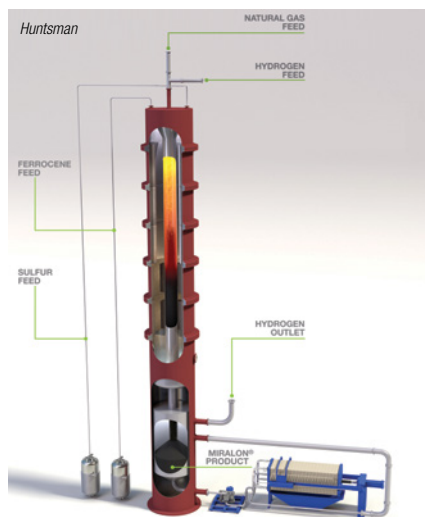
FIGURE 2. Huntsman's Miralon process generates carbon nanotubes, which can be high-value additives for several applications

properties of the solid carbon to suit particular applications, while effectively controlling carbon deposition. "We've really been working at the forefront of science on the chemistry of methane pyrolysis, which is not fully understood," notes Hanson. "Monolith engineers have worked with partners on shock tubes to probe the kinetics of the reaction. Careful investigation of reaction mechanisms and kinetics allows us to address the technical challenges of the process," he says.

A large market for carbon black produced via MP is vehicle tire manufacturing, and Monolith has carefully engineered the process to control carbon deposition for commercially viable time periods, while also ensuring that the carbon black produced has the properties required by the tire industry, Hanson says.

In May 2023, Monolith and Goodyear Tire and Rubber Co. announced that Monolith's carbon black will be used in an all-season passenger-vehicle tire. Tires containing Monolith carbon black have already passed U.S. Dept. of Transportation safety and performance testing. The tires will become available in Q4 2023.

Catalytic reactor approaches

Other approaches to methane pyrolysis employ catalysts for breaking down CH_4 and target the production of high-value forms of carbon, such as carbon nanotubes (CNTs), graphite and others. A number of companies are pursuing this route, including

Hazer Group Ltd. (Perth, Australia; www.hazergroup.com.au), Hycamite TCD Technology Oy (Kokkola, Finland; www.hycamite.com) and Huntsman Corp. (The Woodlands, Tex.; www.huntsman.com).

Huntsman has developed the Miralon process using technology from Nanocomp Technologies, a New Hampshire-based startup it acquired in 2018. Miralon produces H_2 and CNTs as a co-product. CNTs can be used as conductive additives for batteries and thermoplastics, and as mechanical performance enhancers for concrete, rubber and composites.

The Miralon process pyrolyzes methane in a high-temperature H_2 atmosphere in the presence of an iron-based catalyst and adjuvant in a technique known as floating-catalyst chemical vapor deposition (FC-CVD; Figure 2). "The technique drives the CNT growth reaction in a flowing gas stream to avoid the complexities of fixed-bed systems," explains John Fraser, commercial director for Miralon technology and material at Huntsman.

The pyrolysis reaction takes place at temperatures well above 1,000°C. Raw materials are injected into the hydrogen atmosphere in carefully controlled ratios, using the heat to drive the pyrolysis. As the temperature of the gas flow cools, CNTs begin to grow as the free carbon interacts with the catalyst and adjuvant.

The energy to the reactors is delivered using electrical heating. When renewable electricity is available, the resulting H_2 has a carbon footprint up to 95% lower than the current SMR reactors, says Fraser.

The iron "catalyst" used to generate Miralon CNTs is ferrocene, an organometallic compound. The adjuvant is a sulfur compound. Academic studies are underway to examine alternative catalysts, which could potentially increase the carbon-conversion efficiency. "By carefully controlling the stoichiometry of the reactants, as well as temperature and flowrate, the Miralon process preferentially forms CNTs over other carbon forms," Fraser explains.

The reactor uses proprietary methods to keep the carbon away from the reactor walls as much as possible

to prevent deposition, he says.

A unique aspect of FC-CVD is the way the product aggregates in the gas phase as it proceeds through the reactor. "It forms a 'sock,' or aerogel, which flows to the reactor exit for collection. The collection process collapses the aerogel, degassing the product and gradually reducing temperature of the carbon," Fraser says. Once the entrapped gas has been removed, the solid carbon is collected using a proprietary technique.

Miralon CNTs form elongated bundles, rather than individual tubes, and aggregate more than other CNTs. These interconnected bundles give rise to the electrical and thermal conductive properties and deliver improved mechanical properties. Huntsman says the main advantage of the Miralon process over other turquoise H_2 approaches is the properties and value of the carbon product.

Miralon facilities can be co-located where H_2 is used, eliminating transport costs, and sales of CNTs reduce the net cost of the H_2, Fraser says.

He notes that pilot-plant installation is ongoing and is expected to be completed in late 2023. After optimization at pilot scale, Huntsman plans to build a commercial-scale plant, producing kiloton amounts of both Miralon CNTs and H_2. This larger facility is expected to constructed for operations in 2025–2026.

In the case of Hazer Group, research focused on a low-cost, readily available catalyst: raw iron ore, ground to a specific particle size fraction and moisture content. The basic process configuration involves feed gas preheat, followed by injection into the reactor. "Iron ore catalyst is also injected into the reactor and is first reduced predominantly

FIGURE 3. Hazer Group has developed a methane pyrolysis process that uses raw iron ore as a catalyst material

TABLE 1: TURQUOISE HYDROGEN TECHNOLOGY LANDSCAPE		
Company	**Technology summary**	**Level of development and future objectives**
BASF SE (Ludwigshafen, Germany)	Process employs moving dense bed, where carbon particles travel downward against feed gas inside a tubular reactor heated by external induction coils to conduct pyrolysis reaction at <1,400°C. Formed carbon is deposited on the surface of carbon particles	Proof-of-concept lab tests completed in 2019. Ongoing large bench-scale reactor (0.45 kg/hr of H_2). Pilot unit is being designed
C-Zero Inc. (Goleta, Calif.)	Uses a tubular bubble-column reactor filled with high-temperature molten media (molten-metal bottom layer, which catalyzes the reaction, and binary molten salt layer on top to further catalyze the reaction and separate entrained liquid metal). Natural gas feed is bubbled through molten media. Carbon formed inside the rising gas bubbles is entrained into offgas then passed over returning liquid metal on cascading trays before leaving the reactor	Completed proof-of-concept bench scale tests. Pilot plant (400 kg/d of H_2, 10 bars) is scheduled for startup Q4 2023. Commercial demo unit (6,000 kg/d of H_2, 10 MW) is planned to start in Q1 2025
Ekona Power Inc. (Burnaby, B.C., Canada)	Uses pulsed-flow tubular reactor, where feed gas is heated to the reaction temperature by compression resulting from expansion of pressurized combustion gas. The MP reaction takes places in the annulus of closed chamber while combustion takes place inside a concentric perforated tube inside the chamber. After each pulse, the valves on all inlet and outlet lines are open to vent the products and to introduce new batch of reactants	Proof-of-concept testing of 200 kg/d of H_2 bench-scale reactor is in progress. Company is planning to deploy a 1 ton/d plant for field operations in Alberta, Canada
ETCH, Inc., (Baltimore, Md.)	The ETCH process utilizes a thermochemical redox reaction scheme to decompose CH_4 and other alkanes present into C and H_2: 1) $NiCl_2$ sublimation $NiCl_2(s) \rightarrow NiCl_2(g)$; 2) methane decomposition, $2NiCl_2(g)+CH_4(g) \rightarrow 2Ni(s) + C(s) + 4HCl(g)$ at 1,100°C with Ni-C particles also formed; 3) methane pyrolysis $CH_4 \rightarrow C+2H_2$ catalyzed by Ni-C particles at ~1,000°C; 4) separation of Ni-C, Ni, and C from hydrogen; then Ni reaction with HCl under different conditions to regenerate $NiCl_2$: $Ni(s)+2HCl \rightarrow NiCl_2 + H_2(g)$. Any coked carbon on Ni particles gets separated during this step. Recovered $NiCl_2$ is recycled to the process. CH_4 conversion is high (99%+), so PSA is not needed to remove unreacted methane	Completed proof-of-concept and bench/pilot-scale tests. ETCH is planning to deploy trailer-sized 50 m.t./yr of H_2 demonstration scale unit in 2023. Company is working to resolve uncertainty over fate of alkenes
Gasplas (Oslo, Norway) / University of Cambridge, U.K.	Uses a novel, double-vortex, 6-kW microwave (2.45 GHz), atmospheric pressure plasma reactor. Achieved 87% CH_4 conversion, but with high (13% vol.) concentrations of acetylene. Produces graphitic carbon and carbon nanomaterials	Conducting bench-scale tests. Objective is decentralized H_2 production for hydrogen refueling stations using microwave non-thermal plasma (6 kW max), atm. pressures, 450–650 K
Hazer Group Ltd. (Perth, Australia)	Three cascaded fluidized-bed reactors contact iron oxide ore catalyst particles at 900°C with reactive gas mixture flowing upward. The reactors are externally heated using electricity. Graphitic carbon forms on the surface of catalyst particles, which undergo phase-change/attrition, releasing small graphite particles into the reactor offgas. Catalyst surface is thus continuously regenerated, preventing deactivation due to carbon buildup. The offgas is passed through sintered metal filters to remove graphite product. Hydrogen in the filtered offgas is purified using pressure-swing adsorption (PSA)	Completed five technology scaleup steps, including pilot unit. Plan is to demonstrate continuity of operation at a demo plant (100 m.t./yr of H_2; 30X scaleup factor of pilot plant) in Perth, Western Australia fed by biogas. The plant will start hot operations in 2023. Commercial-scale plants are being planned jointly with partners in Vancouver, Canada, Japan and France
HiiRoc Ltd. (Tunbridge Wells, Kent, U.K.)	Combines plasma torch with molten metal reactor. Methane is first decomposed into plasma at 6,000°C and 50 bars using plasma torch connected to molten metal swirl chamber reactor, where recombination into H_2 and C takes place at 800 to 1,000 ºC and 50 bar. Swirling liquid metal functions as a centrifugal separator, separating carbon particles towards the center of the rotating column and downward toward removal port. H_2 gas is withdrawn from the reactor at the top, cooled against the incoming feed in the heat exchanger, and processed further. Carbon buildup inside plasma torch is avoided using hydrogen-purged porous anode in combination with strong vortex flow	Two pilot/demo scale units in operation, third under construction Demonstration/pilot unit (400 kg/d of H_2) in Germany is expected to start in 2023
H-Quest Vanguard, (Pittsburgh, Pa.)	The process uses a proprietary, hardened microwave plasma to pyrolyze CH_4 or other hydrocarbons into H_2 and chemicals or carbon materials. The process can be powered by 2.45-GHz and 915-MHz microwave generators. The process relies on near-instantaneous heating of the gas stream to pyrolysis temperatures and can be configured to produce various high-value carbon co-products, including carbon black and graphene without any catalyst; carbon nanotubes or other materials and chemicals can be optionally targeted with a second-stage catalytic reaction unit, such as a fluidized bed reactor	Deployed a pilot unit in the field in 2023 following completion of bench-scale testing. Commercial target is 1 ton H_2/day with 4 reactor trains (100 kw/915mhz) within a single iso container. Capacity limited by commercially available magnetrons. Scaleup is accomplished by replication. Carbon black is the initial target co-product. Envisioned applications include blending H_2 directly into the natural-gas distribution networks and flaring abatement
Huntsman Nanocomp (Merrimack, N.H.)	Reaction is conducted at 1,150°C in tubular externally heated reactor. Ferrocene and sulfur are added to promote formation of carbon nanotubes, which are separated for agglomeration. These promotors are consumed in the process and are not recyclable. H_2 is purified and partially recycled back to reactor along with hydrocarbons	Completed proof-of-concept bench scale (<1 m.t. of C/yr) tests. Pilot plant (30 m.t. C/yr) construction in progress; operations scheduled for 2023. A demonstration-scale reactor (1,000 m.t. of C/yr) is planned for operation in 2026
Hycamite TCD Technologies Oy, University of Oulu, (Kokkola, Finland)	Thermocatalytic reactor for distributed H_2 generation. Hycamite catalytic process is claimed to be capable of producing carbon nanotubes and carbon fibers while achieving 0.01 kg CO_2 eqv/kg H_2 from plant operations.	Carbomite project is building a pilot-scale H_2 and carbon production plant at the Kokkola Industrial Park. Completed pilot testing
Maat Energy Co. (Cambridge, Mass.)	Technology uses atmospheric microwave plasma (AMP) reactor that incorporates gas-phase catalyst in the plasma region to lower reaction temperature. Commercial magnetrons are used to lower cost. The development efforts were focused mainly on super-dry reforming of methane to produce syngas for synthesis of jet fuels. Methane pyrolysis is being developed to produce supplemental H_2	Lab tests (1 kW and 2.5 kW) were focused on super-dry methane reforming. Methane pyrolysis is more recent. The goal is to produce H_2 at less than $2.00/kg. Objective is to complete 6-kW unit bench tests and build 100-kW pilot unit. Expansion to demonstration scale will be through multiplexing the 100-kW unit
Modern Hydrogen, Inc. (Seattle, Wash.)	Pyrolysis is conducted in a jacketed vertical tubular reactor heated externally by hot fluegas resulting from the combustion of 20–25% of produced H_2. The feed consisting of natural gas mixed with the hydrocarbon recycle stream is preheated before entering the reactor. Methane decomposition is conducted at temperatures >1,100 °C and pressures > 1 atm. It is mainly a thermal process which is mildly autocatalyzed by dispersed formed carbon on a once-through basis (no other catalyst is used) to achieve H_2 yields >85%. Carbon wall deposits are mitigated through proprietary means. Carbon particles entrained in the reactor offgas are separated in a cyclone. Product H_2 is cooled against the feedgas, trim cooled, filtered in a baghouse, and sent to PSA	Developmental bench-scale testing was completed. Two pilot plants are being constructed in Florida and Oregon, with operations commencing Q4 2023. Commercial plant designed for 0.5 m.t./d of H_2 is expected to start operations in 2025 at a customer site. Small distributed applications include H_2 fuel generators for automotive fleets, and small power plants. Analysis predicts H_2 production costs of under $3.00/kg without any carbon sales or carbon offset revenues. Carbon co-product is undergoing testing for use as concrete and asphalt additive
Monolith Inc. (Hallam, Neb.)	Modified Kvaerner/SINTEF process utilizes H_2-blown plasma torch to generate plasma gas (~3,000°C), which is mixed with a portion of the feed gas in the venturi throat between the torch exit and reactor inlet. Remaining feed gas is introduced in stages inside the reactor chamber. The reactor chamber offgas (1,000–2,000°C, 95% H_2) undergoes cooling, carbon separation and H_2 purification. Upon separation, unreacted methane and hydrocarbons are combined with natural gas before feeding the reactor chamber(s). Multiple grades of carbon black can be produced	Demonstration plant (4,700 m.t./yr of H_2) is currently world's largest MP-based carbon black manufacturing plant, and has been in commercial operation since 2020. Full commercial plant (60,000 m.t./yr of H_2) is being constructed, with start of operations targeted for 2026. H_2 will be used to produce synthetic NH_3 onsite. Carbon black will be sold
New Wave Hydrogen Inc. (Vancouver, B.C.)	The process heats methane to decomposition temperature using shockwave compression inside multiple parallel shock tubes comprising a wave rotor reformer. The reaction chamber downstream of the rotor provides requisite residence time. Natural gas pipeline pressure powers the shockwave generation and resulting compression heating. Carbon deposition is mitigated by high turbulence and fast cooling	Bench-scale proof-of-concept tests are underway. Upon completion, pilot plant will be constructed. Designs have been developed for demonstration- and commercial-scale plants
Palo Alto Research Corp., Susteon Inc., (Palo Alto, Calif. and Cary, N.C.)	Methane pyrolysis reaction is conducted inside the hot cyclone reactor, where internal surface is wetted by a descending rotating film of molten zinc that removes carbon particles thrown against the walls by the centrifugal force. Most of carbon floats on the top of descending liquid film and leaves the reactor at the bottom. A separate liquid Zn bottoms stream is withdrawn and returned to the top of reactor after any dispersed carbon is filtered out. A part of the circulating Zn inventory is evaporated and returned to reactor along with the vapor of any residual Zn removed from product carbon. The combined vapor condenses inside the reactor thus supplying the heat necessary for the reaction endotherm and heat loss compensation.	Initial proof-of-concept testing demonstrated at the laboratory scale. Funded by ARPA-E. Improved cyclone reactor concept at the design stage. The plan is to complete tests on this novel concept

by H_2, then cracks methane into H_2 and carbon," explains Hazer chief technical officer Tim Forbes. "The carbon dissolves in the iron catalyst until it super saturates and precipitates as graphite." Graphite and H_2 are cooled and separated with conventional cyclone and filtration technology.

"The catalyst promotes pyrolysis at lower temperatures than would be achieved thermally," Forbes says. "Lower-temperature pyrolysis reduces the risk of reactor-wall carbon formation compared to other thermal processes." Although H_2 production costs will be location-specific and driven by gas and power prices, Forbes says Hazer expects to be competitive with H_2 production via SMR+CCS, and expects to produce H_2 at lower costs than electrolysis, due to drastically lower energy required to split CH_4 compared to H_2O.

Hazer reports that it is nearing the final stages of construction on its commercial demonstration plant, which is anticipated to start up this year (Figure 3). The plant will allow Hazer to validate the performance of its commercial-scale reactor design, and to produce sufficient quantities of graphite for product-qualification activities for applications such as steel production, water purification, batteries, thermal energy storage, and concrete and asphalt blending, Forbes says.

Meanwile, Hycamite has developed its own family of proprietary catalysts that allow the production of H_2 and what the company calls TCD Carbon, a mixture of carbon nanofibers and CNTs, using a carbon-neutral thermocatalytic process that operates at lower temperatures than other pyrolysis processes. Hycamite's process involves gas pretreatment, followed by a reactor for methane breakdown, as well as gas circulation, catalyst regeneration processes, filtration and carbon processing. Hycamite founder Matti Malkamäki says "We have had a pilot plant operational for more than two years, and are now building an industrial-scale demonstration unit with a nominal capacity of 2,000 ton/yr of H_2." Hycamite recently announced an agreement with NW Natural, a gas utility in Oregon, under which the company plans to replicate the demonstration unit in the U.S.

Alternative approaches

Ekona Power Inc. (Burnaby, B.C.; www.ekonapower.com) has taken a different approach. Ekona's patented xCaliber reactor uses the energy from combustion to dissociate feedstock methane into H_2 and carbon. Products of combustion are injected directly into the feedstock chamber to drive the needed heat transfer, temperature and pressure for pyrolysis.

The result is a reactor design that is catalyst-free, low-cost, scalable, and mitigates carbon fouling, according to Gary Schubak, Ekona vice president of business development. The company is currently executing a multi-year development program that will commercialize the technology later this decade. "We have already built and tested a proof-of-concept reactor to validate the design," he says. "Now, we are testing a scaled-up (~200 kg/day H_2) reactor at our facility, which is integrated with key system components for carbon separation, H_2 pu-

rification and thermal management." In 2024, Ekona plans to scale up to a 1-ton/day of H_2 pilot plant with five reactors working together. Ekona's technology targets large industrial applications requiring 100–300 ton/d of H_2 or more. It can be deployed wherever there is natural gas infrastructure, since it does not rely on water, clean electricity or CCS.

Schubak notes that Ekona carried out techno-economic analyses of the process from the beginning to ensure the technology scales and meets industry's priorities. "We believe our solution can produce turquoise H_2 at costs comparable to conventional grey-H_2 processes, while significantly reducing greenhouse gas emissions. Selling the carbon and taking advantage of clean H_2 incentives can significantly improve economics."

Other technologies that are nearing pilot or demonstration stage include molten-media processes, such that from C-Zero (Goleta, Calif.; czero.energy), a chemical redox process from ETCH Inc. (Baltimore, Md.; etchmaterials.com), a plasma torch with molten-metal reactor (HiiRoc; Hull, U.K.; www.hiiroc.com), and a moving-bed reactor (BASF; see Table 1).

The ETCH process employs Ni-based redox reactions and is projected to produce H_2 at \$1.00–1.50/kg of H_2 without any carbon sales or carbon offsets revenue, which compares favorably to SMR. The process has a high H_2 yield (>99%), voiding the need for H_2 purification and hydrocarbon recycle.

The molten-media bubble-column reactor design by C-Zero employs an external chamber filled with molten salt to combust H_2, thus generating heat for the pyrolysis reaction.

TNO Netherlands (The Hague, the Netherlands; tno.nl) is an example of a research-stage, laboratory-scale project using molten metal. The TNO process uses dry-reforming to obtain synthesis gas, from which olefins and sustainable aviation fuel can be made. A key hurdle with molten metal is preventing carbon contamination of the metal. TNO has developed a molten-salt wash section that removes metal from the solid carbon.

Looking forward

Green, blue and turquoise H_2 processes will likely each work better under different sets of circumstances, conditions and geographic regions, and all three types will continue to develop and be deployed, but in the opinion of Monolith's Hanson, turquoise H_2 is the most broadly applicable approach to making H_2 and carbon with minimal CO_2 emissions.

Research groups and institutes will continue to be highly involved in the methane pyrolysis space, with new spin-outs from research groups expected to emerge in upcoming years, says IDTechEx's Idrissov.

For additional information on the commercial development of turquoise H_2, refer to the online version of this article (www.chemengonline.com). ■

Scott Jenkins and Carl Fromm

Newsfront

Modular Construction Encourages New Applications

The efficiency and cost effectiveness of modularity provides advantages for small- and large-scale projects

When the right conditions exist, the benefits of modular construction — from laboratory scale to large scale — are plentiful and allow single-source, cost-effective and efficient construction of new or expansion projects in the chemical process industries (CPI). Furthermore, these same advantages lend themselves well to many emerging applications, permitting new processes to be explored, proven and scaled up so they can get to market faster.

What is modular construction?

Modular construction is a method by which a plant or single process, including all the required process equipment, instrumentation, valves, piping, components, controls and electrical wiring, is fabricated and mounted within a structural steel skeleton, known as a module. Modules are designed, built and tested at an offsite fabrication yard or facility and then transported by truck or barge to the final location, where they are set in place. A module may stand alone or multiple modules may

FIGURE 1. It is not the size of the project that makes it a good fit for modular construction, rather it often has to do with the complexity of the project. Shown here is a complex module designed and built by Wood

be connected to each other or to existing infrastructure. A module may be a small, single skid with laboratory-scale equipment, a single truckable process module or there may be multiple modules that are joined almost like Legos to form a large process system or an entire plant.

When modular makes sense

"There are several advantages to modular construction versus traditional, stick-built construction if it is done in the proper way and with the right approach," explains Giampiero Trivella, senior vice president of process and chemicals, Europe & Africa, and site operations director with John Wood Group plc (Wood; Aberdeen, Scotland; www.woodplc.com). "It is not necessarily the size of the project that makes it a good fit for modular construction, rather it often has to do with the complexity of the project. There are cases where, regardless of the size, it is usually beneficial and less expensive to go with a standard stick-built approach" (Figure 1).

Grant Girouard, business engineering manager with Zeton (Oakville, Ont., Canada; www.zeton.com), agrees: "Modular is not always suitable. For instance, a simple project, such as adding an instrument rack or a system for flow distribution of a chemical that requires just control valves, flowmeters and piping, is something that can be more easily and cost effectively installed on site. In cases where it is not complicated enough to warrant modular construction, you lose the value of going modular."

Additionally, if a project is too large, it may not make sense to go modular. "For truckable modules, the diam-

Koch Modular Process Systems

FIGURE 2. The components in truckable process modules, including columns, vessels and tanks, should remain within a 12-by-14 foot footprint in order to fit on the truck for transportation to the site. Shown here is a process module designed and built by Koch Modular Process Systems

eter of columns, vessels and tanks must fit within a 12-by-14-foot footprint in order to fit on the truck," says Mauricio Villegas, business development manager with Koch Modular Process Systems (Paramus, N.J.; www.kochmodular.com) (Figure 2). "However, if the project really lends itself to modularization except for the diameter of a column or a vessel, we can find a way to incorporate it into the design and ship these for placement next to the module so they may be tied into the process. This is what we call a hybrid module."

The location of the fabrication yard is also an important consideration, notes Wood's Trivella. "Going modular can be more costly or less expensive, depending on the location of the fabrication yard and the cost of labor in that area," he says. "There may be high transportation costs, especially when ships are required for overseas transportation of megamodules. There are times when the cost of labor may be low in the area of the fabrication yard, but the transportation cost to the location may be high, or vice versa, so there is a cost balance that needs to be assessed

FIGURE 3. Thoughtful evaluation of all factors is a necessity when considering modular construction for any size project. Shown here is a modular filter dryer system with integrated contained discharge designed and built by DeDietrich Process Systems

in the early stages when considering a modular project."

Another consideration, especially when dealing with adding a modular process to an existing facility is whether there are site restrictions, says Todd Pollack, engineered systems business unit leader with DeDietrich Process Systems, Inc. (Mountainside, N.J.; www.ddpsinc.com). "You need to be able to bring an entire module into the facility, so if there is not sufficient access, then bringing the equipment in as multiple modules or piece by piece and stick-building it in place may be more appropriate."

He continues to say that thoughtful evaluation of all factors is a necessity when considering modular construction for any size project: "People think they are getting a skid that is dropped off and they just push a button to get started, but that's not realistic, especially with larger systems. There is a defined boundary of scope and other design issues, such as electrical, controls, structural, installation and startup on modular systems, that need to be understood between all parties," says Pollack. "There is no single question to answer to determine if it makes sense to go modular. Every project has different goals, objectives and prioritizations" (Figure 3).

The advantages

Still, experts are quick to point out that in the cases where modular construction is a good fit, if it is properly carried out and makes financial sense, there are several significant advantages.

One of the greatest benefits is the fixed price, says Koch's Villegas. "Modular projects offer a fixed price very early in the design stage that is plus/minus zero for a complete modular system, whereas stick-building projects can be cost reimbursable or convertible to a lump sum halfway through the detailed engineering stage, which can be as far as six months into a project," he explains. "It has been reported that an estimated 25% of stick-built projects fail due to cost overruns. Because modular offers a fixed price, it reduces the risk of cost overruns."

Another noteworthy benefit, says Wood's Trivella, is safety. "Modules are done in a fabrication yard, which is specifically arranged for construction activities and, as such, to be a safer environment than building on site in facilities. Because safety can be more easily managed, laborers are not exposed to the process environment where other units may be in operation and nor are they at great heights."

In addition, using a fabrication yard may also reduce costs. "Because the yard is a controlled environment, it is not exposed to, or at the mercy of, weather and has a consistent workforce. This means you are not bringing in craft labor from different regions, putting them up in camps and paying them per diem, so it is possible to greatly reduce costs. We see an average of 30% overall project savings," says Villegas.

And, because the construction is handled at a dedicated fabrication yard, not on site, it permits a "parallel path," says Zeton's Girouard. "When stick building, the order of operations and logistics can be quite complicated and includes getting permits, preparing the site, coordinating procurement and delivery of equipment and then coordinating the labor. Modular construction allows more flexibility," he says. "You can be in the design stage while permits are obtained, then while the site is prepared, the modular builder can procure and receive equipment and coordinate construction in the fabrication yard, while also condensing the schedule and crew required for construction. Typically, all this can be coordinated

A WORD ABOUT CONTROLS

While the control of modular projects was previously a challenge, automation providers and modular construction firms have stepped up their game, making this concern a thing of the past.

"Conventionally, process engineering systems were set up to precisely control a plant or a process," says Thomas Bertsch, head of process industries, North America, with Festo (Islandia, N.Y.; www.festo.com). "On the plus side, this means they are precise, but on the minus side, it means they are not flexible. The principle of traditional automation works if the required product remains the same in terms of quantity and characteristics. It also means that when new products or processes are introduced, changing conventional control systems takes a lot of time, so in these cases and in the case of modular processes, it makes sense to use a different approach."

Today, he says, experienced automation experts rely on standardized communication between individual modules, which allows a "plug-and-produce" approach. "Think of it like today's consumer electronics, where you have a computer and connect a mouse or keyboard without installing drivers or software. This concept is similar to today's automation for modular designs," says Bertsch.

He explains his company's four steps to automation of modular plants as follows:
• First, process engineering is broken down into sub-processes and a Process Equipment Assembly (PEA) that includes all the mechanical and automation technology components for autonomous operation are defined for each sub-process.
• Step two involves modularizing the automation. Each PEA consists of a decentralized controller, remote-I/O components and pneumatic controls with all field functionalities pre-programmed.
• The PEAs are interconnected to form a process system and each of them provides its specific functionality via an interface that is standardized according to Module Type Package (MTP), which serves as a standardized software interface between the PEA's controller and the process control system of a modular plant. A lean Process Orchestration Layer (POL) coordinates the functionalities in the overall system, while the MTP facilitates smooth and fast integration of the equipment.

Using the modular approach described above, systems can be built according to preferences and current requirements. The Festo MTP-compatible library provides not only all the function blocks defined in the MTP standard, but also some specific pneumatic functionalities. All these functions bring the visualization symbols needed to monitor and the faceplates needed to operate the equipment and help simplify the process of defining complex services. ❑

FIGURE 4. Modular construction firms typically have project managers, procurement, project designers and engineers in various disciplines on site, so anything that needs to be adjusted can be handled in the fastest and most seamless way, which means there is a significant reduction in time to market. Shown here is a turnkey modular system that EPIC designed and built for installation at a customer's facility

so that we are ready to deliver when the site has been prepared."

Koch's Villegas continues to say that this arrangement also provides greater efficiency and productivity during construction. "A typical modular project — including detailed engineering, fabrication and delivery — takes an average of 10 to 15 months to execute, depending on scope and complexity, while the same project, if field constructed, can take 18 to 24 months. So modular construction can typically shave six to eight months off a project's timeline," he explains.

Thanks to parallel scheduling and single-source responsibility, modularization often allows processors to bring projects to market faster, says Kenny Reekie, vice president of sales and marketing with EPIC Systems, Inc. (St. Louis, Mo.; www.epicsysinc. com). "In addition to sequential scheduling and building, modular construction firms typically have project managers, procurement, project designers and engineers in various disciplines on site, so anything that needs to be adjusted can be handled in the fastest and most seamless way, which means there is a significant reduction in time to market" (Figure 4).

Encouraging new applications

The ability to bring a project to market faster and at a lower cost with fewer risks makes modular construction very appealing to new applications, such as those in the sustainability field, which is growing rapidly due to governmental regulations and corporate sustainability initiatives.

"We are seeing a lot of activity in the decarbonization and sustainability space," says Koch's Villegas. "These are small to mid-sized projects, so all the columns and tanks fit within the required space constraints for transportation via truck. In addition, they are looking for the fastest time to market."

Biofuels, bio-based chemicals, recycling of plastics and battery technologies are very popular applications that lend themselves well to modularization. "In addition to being of the right size and offering the required time to market, many of these products compete with an existing hydrocarbon-based product, so there's usually a narrow gap on whether or not the projects are commercially viable," says Villegas. "The margins are thin, but going modular with its cost savings gives them the needed cost advantage to make it work."

In addition, many sustainability-based projects are emerging technologies that are not yet ready for full-scale production, says EPIC's Reekie. "They are interested in modular construction because it makes it possible to cost effectively scale up from R&D to pilot scale and beyond," he says. "As they come out of R&D

FIGURE 5. For applications that have a high-value/ low-volume output, such as designed drugs and semi-conductor chemicals, going modular addresses the need for cost effectiveness and when done via a pre-validated, standardized process module, such as Zeton's ContiUnity technology, it allows a continuous process

laboratories, they want to make sure they have the process refined and can make it at scale without sacrificing the integrity of the product, so they must go through the intermediate step of pilot scale before full-scale production. Many of these projects rely on modularity because it not only allows speed to market, but also provides the flexibility to move the process to different locations and gather data from the process if it is automated properly, which can help further refine the process before going to full-scale production, which can also be accomplished modularly."

Koch's Villegas adds that modular construction is attractive in emerging applications with potential for growth because it also provides repeatability. "Going modular allows performance benefits related to scalability and repeatability. Because many modular designs are made to be interconnected like Legos, we can design systems to be initially delivered as small-scale facilities to meet the current demand and then, as demand increases, we can deliver additional modules that can be bolted on to increase capacity. This is an important advantage in a circular economy and where sustainability projects are concerned."

Modular construction is also beneficial for applications that have a high-value/low-volume output, such as designed drugs and semiconductor chemicals, says Zeton's Girouard. "Not only does going modular address the need for faster time-to-market and cost-effectiveness in these applications, but when done properly with a pre-validated, standardized process module [Figure 5], it allows high-value products to be made in a continuous process, versus as a batch, which is not only more efficient, but also reusable, transportable and contained within a smaller footprint."

With today's current economic challenges and sustainability initiatives, chemical processors of established products, as well as those with emerging products and processes, may find that, under the right conditions, modular construction provides significant advantages. ■

Joy LePree

Facts At Your Fingertips

Wet and Dry Milling

Department Editor: Scott Jenkins

Milling is a common technique for controlling particle-size distribution (PSD) in solid products through size reduction and surface modification. Broadly, mills can be categorized as wet or dry mills, and these two categories are each further subdivided by how comminution is achieved. Wet mills use liquid as their working fluid, whereas dry mills use gas. Common mill types and their characteristics are shown in Table 1. This one-page reference provides a brief review of wet milling versus dry milling.

Wet milling

In wet milling, a slurry containing crystals is directly milled in a rotor-stator device prior to filtration and isolation of the product. The wet mill rotors and stators are composed of walled disks with gaps, called "slots" or "teeth," on the walls. When spinning at a high tip speed, the rotor acts like a centrifugal pump, which moves the solid material in the solvent slurry through the mill and forces flow through the narrow slots, creating transient highly turbulent eddies that constitute the mechanical energy source for particle breakage. Breakage is likely due to force moments transferred from the liquid media to the particles.

Rotor-stator wet mills have historically been used as emulsifiers for water-oil blends, such as for the food or cosmetic industry, but recently have been also utilized for size reduction of active pharmaceutical ingredients. Rotor-stator wet mills often generate fine particles via attrition, with potential negative impact on the filtration rate and broadening of the PSD.

Other examples of wet mills include media mills and cavitation mills. Media mills use spherical beads made from ceramics, such as zirconia oxide, or polystyrene (PS), to reduce particle size. This mechanism involves a sort of grinding, polishing attrition-type action, where the dense and viscous liquid acts to lubricate the beads, as well as to help dissipate the frictional heat generated from the grinding mechanism.

Cavitation mills generate mechanical energy via the dramatic pressure drop that causes cavitation. Extremely rapid evaporation generates transient gas bubbles, which then collapse violently, causing shockwaves to propagate through the adjacent liquid phase to fracture the suspended particles.

Most wet milling, whether rotor-stator or media, is conducted in recycle mode, where the batch slurry is recirculated from the holding vessel through the mill, often for multiple batch turnovers, until the PSD reaches a pseudo-steady-state minimum.

Dry milling

Dry mills operate in a gaseous environment — usually an inert gas like N_2 being either a carrier stream for the pin mill, or providing the mechanical energy for the particle collisions, as in the case of jet mills. Under milling conditions, these gases are at significantly lower density than liquids and are also compressible, so viscous dissipation and dampening forces are lower, allowing particle collisions (with other particles or mill walls) to be the major particle-fracture mechanism.

While this allows for more efficient energy usage, the particles also absorb most of the heat generated by the collisions, which could be problematic for crystals that either have a low glass-transition temperature (Tg).

Milling in a dry environment can also result in more static buildup on the particles, since inert gas is not an effective conductor or carrier of electrostatic charges that are created by the collisions.

Although most dry mills are constructed from metallic materials, some residual charge on milled particles could make them cling to the walls or clump together.

Pin mills have metal pins on both the rotor and stator. And while the rotor spinning at high tip speeds will also cause a vacuum draw and pumping effect that, combined with centrifugal force, transports the particles suspended in nitrogen through the array of pins, the primary mechanism of action is particle collision with the pins.

Jet mills utilize high-pressure gas streams to suspend and accelerate the particles to cause particle-particle and particle-wall collisions.

Although internal geometries and flow patterns differ, jet mills generally share the same mechanism of action: particles in the mill continue to impact the raceway until they are small enough to traverse the path without wall collisions and then leave the mill.

Dry milling exhibits product loss (mostly due to fines entrainment into dust bags and physical losses to the equipment internal surfaces and charging devices like hoppers) of about 5–10%, which is a significant yield reduction.

Dry milling is often conducted in single-pass mode, regardless of mill type. It is difficult for dry mills to set up a recycle-type loop like that for wet mills. The preferred strategy is to select a higher-energy dry mill, such as a pin mill or jet mill when a smaller size is required. ∎

TABLE 1. COMMON MILL TYPES AND CHARACTERISTICS					
Mill type	Wet or dry	Energy input and particle breakage	Characteristic maximum velocity, m/s	Specific energy input to solids	Product size range, d_p
Jet mill	Dry	gas velocity; particle-wall, particle-particle	343 m/s sonic	High	1–5 μm
Media / ball	Wet	rotational speed; media-type particle-ball	Impulse impacts 2–4 m/s	High	<5 μm (depends on bead size)
Pin mill	Dry	rotational speed; particle-pin	37 m/s to 240 m/s	Medium - high	10–20 μm
Rotor-stator	Wet	rotational speed; particle-pin, particle-fluid	20–50 m/s	Medium	10–40 μm
Hammer mill	Dry	rotational speed; particle-hammer	14–30 m/s	Medium - low	<100 μm
Comill	Dry	rotational speed; screen, particle-screen	8–17 m/s	Medium - low	< 100 μm

Hydrogen Production via Methane Pyrolysis: An Overview of 'Turquoise' H$_2$

'Turquoise' hydrogen processes generate H$_2$ without releasing CO$_2$. Presented here are the opportunities and challenges for producing hydrogen by methane pyrolysis

Carl Fromm
Green Star BCS, LLC

Hydrogen-producing processes are classified using a color scheme according to their carbon footprint (Table 1; [1–3]). So-called "turquoise hydrogen" is produced by methane decomposition, which encompasses the following: thermal breakdown of molecular bonds (pyrolysis); non-thermal breakdown using non-thermal plasma (plasmalysis); radiation (photolysis); and chemical splitting (chemolysis) through halogenation or NiCl$_2$ redox reactions [4, 5]. Adjacent H$_2$-producing processes involve pyrolysis of plastic waste, paper and biomass, methane coupling into acetylene, dry methane reforming, hydrogen sulfide splitting and others.
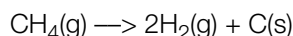
This article discusses the thermodynamics, process configurations and technical challenges associated with turquoise hydrogen production. A companion piece to this article (see pp. 12–16) covers the commercial development of turquoise H$_2$, along with the progress of companies and research organizations that are pushing the technology ahead.

At the present time, turquoise hydrogen is a competitor to incumbent grey hydrogen, produced by steam methane reforming (SMR), and to blue hydrogen, produced by SMR with added carbon capture and storage (SMR-CCS). Compared to SMR, methane pyrolysis consumes twice as much feed to produce the same quantity of hydrogen. However, it does not produce direct CO$_2$ emissions, and offers energy savings, as well as potential revenues from the sale of carbon co-product.

Methane pyrolysis

Methane can be viewed as a hydrogen carrier, like ammonia, rather than as a fuel. The methane pyrolysis (MP) reaction (Equation (1)), also called methane cracking, splitting or thermolysis, breaks methane molecules directly into elemental hydrogen and carbon at elevated temperatures, typically at 600–1,200°C:

$$CH_4(g) \longrightarrow 2H_2(g) + C(s)$$

$$\Delta_R H^0 = 74.85 \text{ kJ/mol } CH_4$$
$$\Delta_R H^{1,000°C} = 91.7 \text{ kJ/mol } CH_4 \quad (1)$$

The MP reaction is endothermic and requires 37.4 kJ/mol H$_2$ at standard conditions, in contrast to th286 kJ/mol H$_2$ needed to produce green H$_2$ by water splitting through electrolysis or thermolysis. It also compares favorably to the 63 kJ/mol H$_2$ required by the SMR reaction combined with the water-gas shift reaction and steam generation for the reformer.

If all H$_2$ produced is combusted, the overall cycle can be viewed as burning off hydrogen only while leaving carbon intact. Combustion of produced H$_2$ yields 484 kJ/mol CH$_4$, which provides 60% of the low heating value of methane (802 kJ/mol CH$_4$), where carbon is fully oxidized to CO$_2$.

The MP process can thermally sustain itself since only 15–25% of available H$_2$ combustion heat is needed to provide the required heat for the reaction. The remaining 75–85% of H$_2$ produced can be exported or used onsite.

Methane conversion yield is promoted by low pressures and higher temperatures, in accordance with La Chatelier's principle. MP reactors are maintained above atmospheric pressure to prevent in-leakage of air anywhere in the process, to minimize reactor size and to speed the reaction.

As for kinetics, the reaction becomes spontaneous at approximately 550°C and attains chemical

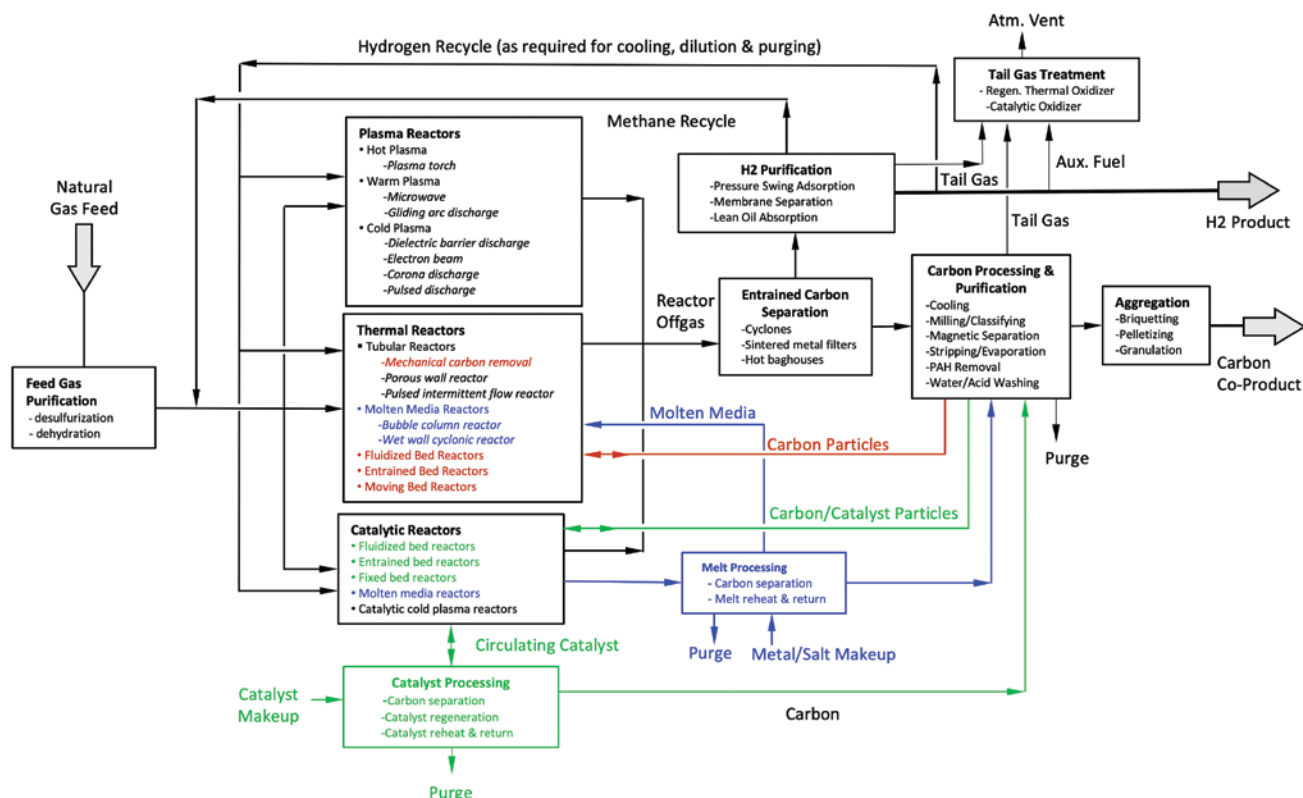| TABLE 1. HYDROGEN MANUFACTURING COLOR CLASSIFICATIONS		
H$_2$ color classification	H$_2$ manufacturing process	CO$_2$ emissions from plant operations, kg CO$_2$ per kg H$_2$ produced
Black	Bituminous coal gasification	18–20 [1]
Brown	Brown coal (lignite) gasification	7–14 [2]
Grey	SMR of natural gas	8–12 [1, 3]
Blue	SMR with CCS	0.4–6.5 [1, 3]
Turquoise	Natural gas decomposition	0–1.1
Green	Electrolysis of water using renewable energy	0

FIGURE 1. This flow diagram shows the elements of a generic methane-pyrolysis process used in manufacturing turquoise hydrogen

equilibrium at higher temperatures (1,300°C+) and higher pressures (>1 atm). Reaction rates at lower temperatures are relatively slow, so the overall conversion is kinetically limited. For this reason, considerable research efforts have been invested into developing catalysts capable of speeding up the reaction at lower temperatures.

For initial reactor sizing and determining the overall CH_4 conversion, the MP reaction rate, r, can be expressed through a simple first-order kinetic equation:

$$r = -d[CH_4]/dt = k[CH_4] \qquad (2)$$

where the reaction rate constant, k, is given by the Arrhenius equation.
$$k = A \, exp \, (-E_a/RT) \times [CH_4] \qquad (3)$$

The pre-exponential factor A and the activation energy E_a are determined experimentally and can be found in literature for specific reactor configurations. For example, Becker and others [6] present a compilation of A and E_a values for various reactor types.

Equation (1) does not account for reactive species, such as acetylene, ethylene, ethane and higher hydrocarbons, along with CO_2, H_2O and mercaptans that may be present in natural gas. To account for these species, schemes involving simultaneous reactions were developed (see the online version of this article at www.chemengonline.com).

Natural gas (NG), the main source of methane, is widely available through the existing 3-million-mile long pipeline infrastructure in the U.S., which is a significant plus for wide-ranging MP deployment. By contrast, transporting H_2 from centralized production facilities to potential users will require huge and challenging expansion of the existing 1,700 mile-long H_2 pipeline infrastructure.

The greenhouse gas emissions (GHGE) that originate within the MP plants include fugitive NG leaks and combustion of tail gas from H_2 purification operations. Offsite GHGE originate in upstream NG production, transport and storage operations, and involve NG leaks, flaring and combustion to generate heat for NG purification, power for pipeline compressors and associated fossil-fuel power plants. Operating plant emissions can be easily exceeded by offsite emissions, which stresses the importance of eliminating NG leaks everywhere in the supply chain, using power from renewable energy sources, or generating plant power onsite using H_2.

In the context of offsite impacts, it is worth noting that MP can remove CO_2 from the atmosphere if the feed is biomethane obtained by anaerobic decomposition of biomass, such as landfill gas, anaerobic digestor off-gas from green waste decomposition or from municipal and industrial wastewater treatment.

Reaction products
As stated above, the main products of the MP reaction are H_2 and solid carbon. The main uses of H_2 include:
• A reactant for production of basic chemicals (such as ammonia), petroleum refining, reduction of metal oxide ores, hydrogenation of fats and other processes
• A clean (no carbon emissions) fuel for processes requiring high-temperature heat, such as ore smelting, calcination, manufacture of cement, glass, ceramic materials and others
• A clean fuel for electric power generation and for propulsion of ships, locomotives and aircraft using either direct combustion or fuel cells. Automotive use is limited by lack of large-scale H_2 distribution infrastruc-

ture, although this can be changed by distributed modular MP systems

Produced elemental carbon can be used commercially as a filler for tire rubber and plastics, a pigment for ink and coatings, an adsorbent, a reducing reactant for pyrometal-lurgical applications, for electrodes manufacturing, and more recently, as a filament for production of structural polymers using carbon fibers, nanotubes (Figure 2) or graphene.

If the MD process is deployed on a large scale commensurate with the current H_2 world-wide demand (around 97 million metric tons H_2/yr), the solid carbon produced (294 million m.t./yr of C) would far exceed current combined demand for carbon black, graphite, metallurgical coke, and anode coke (50 million m.t./yr of C). Unless new high-volume commercial uses are established, this huge excess of 244 million m.t./yr of C would have to be land-disposed (for example, in abandoned mines). This problem would be exacerbated if future demand for H_2 is increased — for example, replacing coke with H_2 in steel manufacture can increase H_2 demand by 90 million m.t./yr alone.

Perpetual storage of solid carbon does not pose the risk of CO_2 releases associated with CCS, which involves transporting and storing of liquefied or supercritical CO_2 under pressure in geological formations. Instead, the risks include carbon dust explosions and potential toxicity due to presence of residual carcinogenic polycyclic aromatic hydrocarbons (PAH). Fortunately, both of these risks can be mitigated. Unlike CO_2 pipelines required for CCS, transportation infrastructure for bulk solids is firmly in place. Also, filling empty mines with carbon could preserve some coal-mining jobs.

Process configuration

The block flow diagram shown in Figure 1 shows a generic MD process and outlines various technology alternatives. Brief descriptions of the process steps follow.

Feed purification. Pipeline-quality natural gas feed may be treated with zinc oxide (ZnO) to remove odorant mercaptans and any residual H_2S

prior to reaction to avoid metal catalyst poisoning. For thermal or carbon-catalyzed reactors, the desulfurization step is not necessary, since minor amounts of H_2S and mercaptans in the feed actually promote methane decomposition in the presence of carbon [7]. In general, small concentrations of C_2 to C_{6+} hydrocarbons, CO_2, N_2 and H_2O should not significantly affect the methane pyrolysis process, although their process fate, such as methane-water reactions leading to CO or CO_2 formation, needs to be considered in the overall process design. One concern arises if C_{2+} hydrocarbons are present in NG at higher concentrations, which could lead to excessive carbon deposition. Mitigation measures may include pre-pyrolysis reactors [8].

Methane pyrolysis reactors. Methane pyrolysis reactors can be grouped into three categories: plasma, thermal and catalytic. Table 2 contains descriptions of each reactor type.

Entrained carbon separation. Carbon particles entrained in the reactor exit gas can be separated using cyclones, sintered-metal filters or high-temperature baghouses equipped with ceramic filter elements.

H_2 purification. In this step, H_2 is separated from unreacted CH_4, C_{2+} hydrocarbons and other species present in the filtered and cooled reactor offgas. The separated hydrocarbon-rich stream is recycled back to the reactor. Separation processes include pressure-swing adsorption (PSA), membrane separation and lean oil absorption/desorption. These processes can also be used to remove non-hydrocarbon species (such as N_2, CO_2, H_2S and H_2O) from the reactor offgas. To prevent their buildup, the hydrocarbon-rich recycle stream must be purged, or a separate stream containing these compounds would have to be generated (for example, through staged PSA depressurization and purge sequence).

A portion of the purified H_2 may be recycled back to the process for plasma-gas generation and/or cooling, heating, dilution or purging needed to minimize carbon deposits on feed-gas injection nozzles or reactor walls.

Tailgas treatment. Since the purge

TABLE 2. METHANE PYROLYSIS REACTOR TYPES	
Reactor type	**Description**
Plasma reactors	Plasma reactors consist of both thermal (hot) plasma and non-thermal plasma reactors. In hot plasma reactors, the feed gas is heated to high temperatures (<2,000ºC) by an electric arc inside a plasma torch either directly or by mixing it with hot (<6,000ºC) plasma gas generated by passing H_2 through a plasma torch. Methane chemical bonds are broken by thermal vibration and excitation. Plasma gas is mixed with part of the incoming feed and routed to the reaction chamber, where it is mixed in stages with the remaining feed gas. The reaction chamber provides residence time for recombination of formed free radicals and ions into final reaction products. In non-thermal plasma reactors, the feed gas is typically heated to 700–900℃ by passing it directly through either "warm" plasma (1,000–6,000ºC) generated by microwaves or by gliding arc discharge, or "cold" plasma generated by dielectric barrier discharge, electron beam, pulsed discharge or corona discharge. In non-thermal plasma reactors, C-H bond breakup is aided by interactions with high-energy (high-temperature) electrons. Methane conversion and reaction product composition depend on plasma generator type.
Thermal reactors	Thermal reactors typically operate at 1,000 to 1,200ºC to provide acceptably fast thermal and mainly non-catalytic CH_4 decomposition using the following configurations: •Tubular reactors, where flowing gas mixture is heated by reactor walls that are kept hot by external heaters or hot fluegas from H_2 combustion •Fluidized-bed reactors where reactions occur both in the reacting gas mixture and on the surface of fluidized particles. Typical configurations employ bubbling beds where most of the gas is contained in the bubbles rising through dispersed particle (emulsion) phase. The heat is delivered by hot reactor wall or by a side stream of solid particles circulated through an external heater •Entrained-bed reactors (also known as fast bed, spouted bed or riser reactors) employ a lift tube (riser) inside which the reacting gas mixture and entrained particles rise together and empty into a separation chamber. De-entrained particles descend in the annulus surrounding the lift tube to be removed at the reactor bottom. Some fraction of particles is recycled back to the lift tube before removal •Moving-bed reactors where a downward-moving dense bed of particles is in direct contact with an upward-moving gas. External induction coils heat the reactor wall around the reaction zone, although other heating methods can also be used •Molten-media reactors where a reacting gas mixture is bubbled through a pool of molten metal or salt (or both) heated by electric immersion heaters, by hot reactor wall, or by an external melt circulation heater. Configurations include (a) bubble column reactors where carbon formed inside the rising gas bubbles accumulates on top of the melt and is removed through an overflow, (b) wet-wall cyclonic reactors where the descending rotating melt film removes carbon from the reactor, and (c) capillary slug-flow reactors
Catalytic reactors	Catalytic reactors use a catalyst to accelerate MP reactions, promote CH_4 conversion at lower temperatures (<1,000ºC), and improve selectivity toward H_2 and/or toward the desired form of carbon. Catalytic reactions can be conducted in tubular reactors, fluidized bed reactors, or in molten media reactors

or the tailgas may include small amounts of hydrocarbons, CO, or H_2S, direct atmospheric discharge may not be acceptable without treatment using either regenerative or recuperative/catalytic oxidizers. To minimize carbon footprint, high energy efficiency is required, and produced H_2 should be considered for auxiliary fuel.

Carbon processing and purification. Separated carbon that exits the reactor, cyclone, or filter as a dense particulate stream may require cooling prior to subsequent steps. This can be performed in bulk solids coolers employing vertical plate or tube coil exchangers, rotary coolers or jacketed augers.

Size reduction using high-velocity gas jets, micro-pulverizers, or continuous ball, rod or pebble mills, along with the particle size classifier and recycle may be necessary to produce particles suitable for recirculation back to a fluid-bed or to a moving-bed reactor after reheating.

Carbon co-product may have to be stripped of adsorbed H_2, H_2S, CH_4 and larger hydrocarbons to alleviate safety concerns in downstream handling. Stripping may be performed using steam-blown or air-blown rotary drums or fluid beds. If reducing residual PAH concentrations is desired, carbon can be heated to high temperatures to volatilize and/or pyrolyze PAH while stripping lighter species. Alternatively, PAH may be removed using solvent extraction [9] and possibly recycled back to the MP reactor. Stripper off-gas should be routed to the tailgas treatment before atmospheric venting.

Carbon particles removed from molten media reactors may be contaminated with salts or metals, which can be removed by evaporation in a rotary kiln or in a tunnel furnace. Water-soluble salts may be removed by a water washing cascade with an evaporator/crystallizer to recover the salts, and a dryer to dry washed carbon product. Metal contamination may also be removed by particle-size classification, magnetic separation or acid washing.

Carbon aggregation. In this step, fine carbon particles are aggregated to mitigate dusting from subsequent solids-handling operations and the associated safety and environmental concerns. Particle size can be increased through briquetting, extrusion granulation or pelletizing after addition of suitable binders. Other steps may be required for carbon nanomaterials.

Melt processing. This step is needed for molten-media reactors to remove any carbon and impurities present in the melt to prevent their accumulation to unacceptable levels. While carbon can be removed by melt filtration, dissolved contaminants may require purging, which necessitates makeup or periodic replacement. Purged molten metal can be solidified and recycled offsite. Purged salt may have to be disposed of as process waste. A melt circulation loop with a reheater and electromagnetic pump can be used as a heat carrier, although heating coils placed inside the reactor can also provide this function.

Catalyst processing. Catalyst mixed with carbon is withdrawn from fluidized- or moving-bed reactors as a dense particle stream. Processing may entail milling followed by separation of carbon and catalyst through sieves or particle-size classifiers. It also can include catalyst regeneration, whereby carbon deposits are burned off or gasified using steam, and catalyst reheating prior to recycling back to the reactor. Catalyst purge and makeup are also performed at this step. Molten-media catalysts require purification, purge and makeup (see melt processing). The recirculating catalyst stream can be reheated before returning to the reactor to serve as reaction heat carrier.
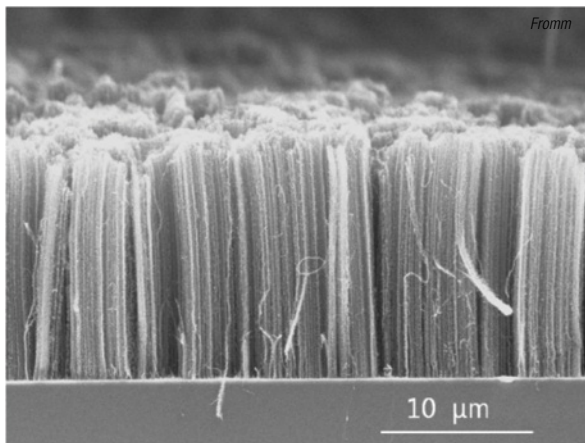
FIGURE 2. Methane pyrolysis processes can produce several forms of carbon, such as carbon nanotubes, like those shown here

Technical challenges

The MP process poses technical challenges. Four of the main ones — carbon deposition, slow reaction, delivering heat to the reactor and heat recovery — are discussed below.

Carbon deposition. Carbon deposition on internal surfaces of tubular reactors leads to reactor plugging and unstable operation. Fouled reactors must be periodically shut down to remove carbon deposits from the walls and feed-gas injectors, and replacing or regenerating the fixed bed of catalyst. This necessitates the use of multiple parallel reactors to maintain production continuity, which adds cost and considerable complexity to the process.

Mitigation approaches include the use of a wet-wall reactor, where the internal reactor surface is wetted by a rotating or falling film of liquid metal or salt [10], a porous-wall reactor (in the context of methane chlorination leading to hydrogen and carbon) [4], or using less adherent surfaces, such as calcium-oxide wall coating to facilitate mechanical carbon-deposit removal [11] or ceramics, including alumina, MgO-C, or SiC [8].

Carbon buildup in plasma torches was addressed by the company Hii-ROC (Hull, U.K.; www.hiiroc.com) by using H_2-purged porous anodes in combination with vortex flow inside the torch chamber [12].

Ekona Power Inc. (Burnaby, B.C.; www.ekonapower.com) developed a pulsed intermittent-flow reactor where carbon deposition is mitigated by strong turbulence associated with rapid depressurization and high-velocity gas flow [13]. Nonrecoverable ferrocene $Fe(C_5H_5)_2$ and sulfur adjuvants have been used to promote carbon nanotube formation without carbon wall deposits in a downflow tubular reactor tested by Huntsman (The Woodlands, Tex.; www.huntsman.com) for production of Miralon, a carbon nanotube material [14, 15].

Prevention of carbon buildup led to the development of fluidized-bed reactors, moving-bed reactors and bubble-column reactors, all of which are being actively pursued by commercial firms. In the fluidized-bed reactors, carbon preferentially forms on the surface of fluidized particles which grow in size and are continuously removed from the bed by gravity-settling below the gas distributor or using an internal overflow weir near the top of the bubbling fluid bed, as in the process developed by Pacific Northwest National Laboratory (PNNL; Richland, Wash.; www.pnnl.gov) that uses fluidized iron-based catalyst [16].

Alternatively, fluidized catalyst particles can undergo attrition and phase transformation inside the bed, releasing accumulated carbon in the form of fine particles that are entrained into reactor gas and then elutriated out of reactor, as is done in the Hazer Group Ltd. (Perth, Australia; www.hazergroup.com.au) process that uses iron ore catalyst in multistage fluidized-bed reactors [17].

In the moving-bed reactor being developed by BASF SE (Ludwigshafen, Germany; www.basf.de) [18], a dense phase of carbon particles moves downward countercurrent to the gas flow inside a cylinder equipped with the hot wall reaction section heated by external induction-coil. Hot solid carbon particles exchange the heat directly with the reacting gas moving upward. Carbon particles grow due to deposition of formed carbon on their sur-

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face which, along with the wall shear forces, prevents carbon deposit on the reactor walls.

Bubble-column reactors mitigate carbon deposition, as the reactions take place inside gas bubbles rising through a pool of molten media, such as metals (Sn, Pb, Ga, Te, Ni-Bi, Cu-Bi, Ga-In-Sn) or salt (KBr, NaBr, NaBr/KBr, NaF, KCl, NaCl, $MnCl_2$), acting as heat transfer fluids at 900–1,400ºC and often as catalysts. Molten media is contained inside a cylindrical reactor that may be provided with a submerged packed bed of ceramic rings or sprays in the vapor space to increase liquid-gas interface. Carbon wall deposits are mitigated by carbon formation at the bubble-liquid interface, which keeps it contained inside the bubble. When rising gas bubbles burst upon reaching liquid surface, carbon is released and floats on the melt surface, from where it can be continuously removed using an overflow weir or gas flushing.

Slow reaction. As discussed above, the methane pyrolysis reaction is relatively slow. While raising the reaction temperature helps, when temperatures exceed 1,300ºC, the equilibrium yield of H_2 starts to decrease due to the formation of acetylene, ethylene and ethane. Moreover, higher temperatures result in higher net energy consumption. To lessen the residence time and the reactor volume, it is possible to increase reactor pressure, but at the expense of H_2 yield. For these reasons, reactor design must carefully examine H_2 yields and exit gas compositions as a function of reaction temperature and pressure along with staged feed-gas injection and staged dilution/cooling with H_2. Multiple competing reactor configurations need to be analyzed using kinetic modeling to optimize the reactor design.

Various catalysts have been developed to accelerate MP reactions at lower temperatures (<1,000ºC) and to improve selectivity toward H_2 and desired allotropic form of carbon; these include the following:

• Solid catalysts, such as metals (Co, Fe, Ni, Si), metals/alloys with promoters/dopants (Ni-Cu, Ni-Pd, Ni-Mo, Ni-La, Ni-Cu-Co, Ni-Sn, Fe-Co, Fe-Mo, Zn-Cu) supported on silica, alumina or carbonaceous materials, metal oxides (FeO/Fe_2O_3, La_2NiO_4), metal carbides (Fe_3C, Ni_3C), and metal-carbon nanostructures (Ni-C)

• Molten-media catalysts, such as liquid metals (Te, Ni-Bi, Ga, Pb), liquid salts (NaCl, KCl, $MnCl_2$, $NiCl_2$, NaBr, KBr, Na_2CO_3, K_2CO_3, Li_2CO_3, or their mixtures), liquid salts with dispersed solid catalyst particles in the form of finely divided elemental metals (Ni, Mo, Mn, Co, Fe, Zn, Ti, Cu), their oxides, carbides or their mixtures, and carbon catalysts (activated carbon, carbon black, graphite and formed carbon). A recent comprehensive review of MP catalysts was conducted by McConachie [8].

Relative to solid catalysts, molten-media catalysts are not prone to carbon buildup. However, their stability is affected by high temperature. Metal catalysts' activity depends on the metal (Ni>Co>Fe) and exceeds that of carbon catalysts [7]. Rapid solid catalyst deactivation caused by carbon buildup, poisoning and sintering is the key concern. Susceptibility to deactivation is higher for Ni-based catalysts than for Fe-based and carbon-based catalysts.

Conventional reactivation of solid metallic catalysts removes carbon deposits using oxidation or steam gasification, and results in CO_2 emissions. This is avoided in the process developed by PNNL, where bimetallic Ni-Cu catalyst on a carbon nanotube support is used to pyrolyze methane at 600°C inside a fluidized bubbling-bed reactor [16]. Formed carbon accumulates on catalyst particles, which are withdrawn from the bed, cooled and acid-washed to separate formed carbon from metallic catalyst precursors. Catalyst precursors are then used to resynthesize the catalyst for recycle back to the reactor. The catalyst can be formulated to increase selectivity toward formation of carbon nanotubes.

Iron-based solid catalysts are more stable and deactivate at slower rates than Ni-based catalysts. The process developed by Hazer Group uses fluidized iron ore (Fe_2O_3/FeO) catalyst particles [17]. Carbon forms as graphite on the surface of catalyst particles, which undergo continuous attrition through intergranular breakup, releasing small graphite particles into the reactor offgas. Catalyst surface is thus continuously regenerated, preventing deactivation due to carbon buildup. Separation of elutriated solid catalyst from carbon is one of the challenges in such systems.

As previously mentioned, special once-through non-recoverable "catalysts" have been used to promote carbon nanotube formation in tubular MP reactors. These include ferrocene $Fe(C_5H_5)_2$ and sulfur additives. Use of ferrocene and iron pentacarbonyl $Fe(CO)_5$ was investigated for the production of hydrogen in solar-heated reactors [28].

Carbon catalysts are considerably less expensive, but also are less active than metallic catalysts, leading to higher operating temperatures (800–1,000ºC) and longer residence times to achieve equivalent conversion. Amorphous carbons (carbon black, activated carbon) are more active than ordered forms, such as graphite. Advantages for carbon catalysts over metallic catalysts include negligible toxicity, high stability, longer lifetimes and no susceptibility to sulfur poisoning, which makes desulfurization of the natural gas feed unnecessary.

Regeneration of carbon catalysts may be performed through gasification with steam, which generates CO_2 and H_2. However, this is not needed for the once-through use of imported carbon catalyst with higher activity, such as activated carbon. Also, it may be preferable to rely on autocatalytic properties of formed carbon product instead of a once-through use of imported catalytic carbon, as practiced by Modern Hydrogen Inc. (Bothell, Wash.; www.modernhydrogen.com).

Low catalytic activity of formed carbon can be compensated for by increasing the circulation rate of carbon product through the reactor, which increases the exposed particle surface area within the reactor.

Methane decomposition can also be achieved through photolysis using heterogenous photocatalysts inside fixed-bed tubular reactors with transparent walls illuminated by external light.

Delivery of heat to the reactor. In addition to the enthalpy required by the endothermic MP reaction, sen-

sible heat is needed to get the reactants to the desired temperature. The overall reaction heat requirement depends on the size of the recycle streams, and can amount to 1.2–1.5 times the reaction endotherm.

In plasma reactors, the heat requirement is provided by electricity powering a plasma generator. Hydrogen or staged feed-gas injection can be used to control the temperature profile. No additional heat source is required.

In non-plasma small-scale experimental reactors, heat is typically delivered to the reacting mixture through a hot reactor wall, whereby the reactor is placed inside an electric furnace or heated using external resistors or induction coils. Such a scheme does not scale up well with growing reactor diameter, because the radial temperature gradient becomes very steep and efficient heat transfer becomes more difficult.

To circumvent scaleup issues associated with externally heated reactors, pilot- and demonstration-scale plant design should consider a circulating side-stream of molten metal or salt, carbon particles or catalyst particles, as a heat carrier. Circulating stream(s) would be withdrawn from the reactor, processed as necessary, reheated and recycled back. External reheaters can utilize resistive, induction and microwave heating, electric arc furnace, H_2-burning fired heaters, concentrated solar heating or immersed plasma torch (molten media only).

Using combustion heat to provide MP endotherm was explored by Muradov [27], whereby a small amount of oxygen is added to a fluidized-bed catalytic reactor employing carbon and iron-based catalyst. Emissions of CO_2 would still be 3–5 times smaller compared to the conventional SMR process. A similar approach is used by C-Zero, whereby H_2 is combusted to heat a circulating molten media inside a bubble column reactor.

Other schemes of delivering heat to reactors are being researched. One of them under development by Palo Alto Research Center [19] involves condensation of zinc vapor to supply the reaction heat inside a molten zinc cyclone reactor. A scheme proposed by Munera-Parra [20] uses chemical energy obtained through exothermic recombination of molecular hydrogen from plasma-generated atomic hydrogen. A novel method utilizes compression heating of methane to pyrolysis temperature using a supersonic shock wave generated by wave rotor reformer technology [21]. Microwave heating of fluidized bed was patented by H-Quest [22].

Heat recovery. The overall heat requirement can be significantly reduced by using heat recovery from reactor outlet streams, or by utilizing waste heat from adjacent processes (for example, from cooling of steel and slag in steel production served by dedicated MP installations) [29].

Heat can be recovered by preheating the feed stream (natural gas mixed with methane recycle) and H_2 recycle stream against the reactor exit streams. Caution must be exercised to avoid coking inside heat exchanger tubes due to overheating of the feed stream.

Owing to the high heat capacity of H_2, most of the heat leaving the MP reactor (~80%) is carried by the gas with the remaining 20% carried by carbon. The entire reactor offgas stream can be sent through a shell-and-tube heat exchanger prior to the solids separation step, as practiced in some carbon black plants. Alternatively, hot carbon is separated in a cyclone or inside the reactor, prior to heat recovery from the solids-free gas through steam superheating, followed by steam generation, and followed by an economizer. Heat can be recovered from carbon using a bulk solids cooler equipped with a vertical plate or coil-tube exchanger.

Superheated steam can be utilized in a combined-cycle cogeneration system employing H_2-fueled gas turbine to generate power for the plant, as well as for export. Such a system would also provide operational flexibility to accommodate swings in external H_2 demand.

MP process economics

Publications dealing with techno-economic analysis of MP technologies use a wide-ranging set of assumptions, methodologies, plant capacities and unit pricing of natural gas, carbon, electricity, water, consumables, labor, carbon-offset credits and other parameters. Because of this variability, the published data do not allow for equitable comparison of projected economic performance of competing technologies. Nevertheless, reviewed articles provide valuable insights into expected economic performance of methane pyrolysis technology and are summarized as follows (for uniformity, all costs are expressed in 3Q 2023 dollars):

• Hydrogen production costs using SMR-CCS technology varied from $1.40/kg to $2.50/kg of H_2, depending on natural gas cost and other factors used in analysis [23, 24, 16]

• For molten salt (KCl-MnCl$_2$) bubble-column reactors, projected H_2 production cost is $1.80/kg of H_2 based on natural gas at $2.30/GJ and zero revenue for produced carbon [24].

• Hydrogen from molten media (Ni-Bi metal and salt) reactors costs $1.70/kg of H_2 to produce, which is much less than water electrolysis based on polymer electrode membrane (PEM) technology ($3.00/kg H_2 for electricity cost alone). A carbon-offset credit of $26/ton CO_2 is required to achieve cost parity with SMR. Alternatively, carbon co-product revenues would have to exceed $200/ton carbon for the same effect [25].

• For fluidized-bed reactors using solid Fe-based catalysts, projected H_2 production cost was $3.20–3.50/kg H_2 based on natural gas at $7.50/GJ, with zero revenue for produced carbon, and no catalyst recycle or carbon purification, all against $2.50/kg H_2 for SMR-CCS benchmark. For H_2 to become competitive with SMR-CCS, 20% of produced carbon would have to sell at $1.20–1.50/kg. The economics and thermal efficiency are highly sensitive to catalyst activity and resulting H_2 yield [15].

• Carbon co-product revenue in the $600–900/ton range will completely offset H_2 production cost [26].

• The H_2 production cost from a fluidized-bed MP reactor will match that of an SMR process (without CCS) if carbon sells for $300–800/ton [27].

• Production cost of H_2 from the MP process based on a hot cyclone reactor wetted by liquid Zn metal is $2.50/kg of crude (94%) H_2, and $3.40/kg pure (99%+) H_2 with zero carbon revenues for both cases [19].

Overall, turquoise H_2 can be produced at $1.80–4.00/kg without carbon sales or offsets, which is not yet cost-competitive with grey H_2 ($0.90–3.00/kg to produce). However, turquoise H_2 may compete favorably with blue hydrogen produced at $1.40–2.50/kg by SMR-CCS.

The economic feasibility of turquoise hydrogen can be vastly improved by selling carbon co-product and generating revenue from carbon-offset credits or from avoided carbon tax (for example, obtained by replacing SMR or oil-derived carbon black plants with an MP process).

Economic feasibility can also be improved through technical innovation. For example, the ETCH process [5] that employs Ni-based redox reactions is projected to produce H_2 at $1.00–1.50/kg of H_2 without carbon sales or carbon offsets revenue, which compares favorably to SMR.

Current growing demand for carbon black and graphite creates significant market opportunities for MP-produced carbon. However, new markets for carbon are needed to strengthen the driving force required for broad adoption of MP technology.

Large-scale grassroots MP plants will have to compete with fully amortized existing H_2 plants. For this reason, it may be worthwhile to consider the feasibility of retrofitting the existing installations with MP reactors and solids handling subsystems.

For more information on MP, view the online version of this article at www.chemengonline.com. ∎

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Management and Maintenance Strategies for Valves

Asset criticality and risk are primary among the many factors that must be considered to appropriately manage valves throughout their lifecycle

Tacoma Zach
MentorAPM

Asset strategies usually define how assets will be treated in the different phases of an asset lifecycle, from acquisition through disposition, and also typically will include corrective action for deficiencies. For example, valves not yet installed will have a set of engagement strategies that differ from in-service valves, as well as decommissioned valves prepped for sale, versus disposition of the asset (Figure 1).

On the other hand, preventative maintenance (PM) strategies are a subset of asset strategies that focus specifically on failure prevention — this includes filter replacements, visual inspections, oil changes and analysis, vibration analysis and the resulting interventions to forestall a decline in performance. Valve PM strategies and their relationship to overall asset strategies are the focus on this article.

Both asset and PM strategies are influenced and informed by several factors in an asset portfolio, listed below. The most important place to start is considering an asset's criticality and risk rankings, because these dictate the focus of efforts more than any other factors.
- Criticality (generally static)
- Risk rankings (will change quickly or slowly, depending on failure type)
- Asset condition
- How assets fail (failure modes)
- Overall design and interconnectedness
- Redundancies
- Mandated level of service
- Operational philosophy

Asset criticality informs strategy

Asset criticality will influence the PM strategies (the "what" and "how often") and the degree to which intervention must happen ("how much" and "how fast" one responds).

Any criticality and risk analysis results should direct focus to the most important assets — those with the highest risk or highest critical-ity. A new, highly critical valve can quickly become a high risk if it is neglected, and such a high-risk asset can greatly jeopardize plant objectives. Low-risk assets can be deferred or assigned a run-to-failure designation.

Intervention strategies based in part on criticality are often broken into three broad categories where the asset's criticality ranking will inform the strategy, described below.
- High-criticality valve assets can never go out of service without sufficient lead time to plan for and supplement the outage
- Medium-criticality valve assets usually require sufficient lead time to minimize outages
- Low-criticality valve assets require awareness that the asset is out of service (failed) and a suitable intervention will be planned as time permits

High-criticality asset strategies. For these valves, asset performance can never fall below a certain level — their performance is essential or critical. High-criticality assets should never fail without prior knowledge and planning. These valve assets need an appropriate level and type of monitoring to understand what is happening to the asset well before an impending failure, in order to allow enough time to plan and schedule a suitable intervention. This may require online monitoring or very frequent in-person condition monitoring of dominant failure modes and frequency of valve failure. It may also require frequent

TABLE 1. MONITORING AND INSPECTIONS BASED ON CRITICALITY	
Description	**Minimum criticality number requiring action**
Run-to-failure or fix-at-will	<2.5
Regular calendar inspections	2.5
Regular condition monitoring	3.5
Continuous condition monitoring	4

FIGURE 1. Whether dealing with brand-new valves, critical in-service valves, uninstalled spares or decommissioned valves, it is important to specify the best plan to keep valves well-maintained

PM routines to maintain the asset in excellent working condition to meet the operational requirements. A suitable intervention may require immediate action, such as the staging of supplemental equipment to carry the lost load or finding alternate means of meeting service levels.

Medium-criticality asset strategies. These valve assets can only be out of service for a short period of time, otherwise mitigation of resulting issues might be necessary. While their performance is important to the overall facility or process objectives, their outage will not endanger the level of service targets in the short-term. In this case, sufficient monitoring is required to plan for the outage and schedule it accordingly, so that the outage occurs within an acceptable timeframe.

Low-criticality asset strategies. These valve assets can be run to failure and repaired at will and should not be on any remote or automated monitoring program. Typical exam-

ples of this type of equipment are non-essential valves, such as ancillary valves, non-process-central valves, secondary support-system valves, and even certain bypass valving. Repair is made to these assets when convenient.

Based on a criticality ranking from 0 to 5 (where 5 is most critical), Table 1 shows an example of a typical monitoring and inspection table that might be used at a processing facility. Anything with a criticality ranking over 4 requires continuous monitoring.

Asset condition

Traditionally, asset condition has been seen as the single most important driver of strategies. While condition plays a part insofar as it influences short-term risk of failure, it must be used cautiously, since it is not the only influence on risk of failure. Much more broadly, condition drives the specific need for repair, not necessarily the strategy or priority, and this is an important distinction. Broken low-criticality valves are a lower priority than a high-criticality valve about to fail.

Failure modes and degradation

A failure mode refers to the ways an asset can break down or fail. The ways an asset fails depends on its components. For maintenance considerations, an asset is actually just a collection of failure modes to be managed. If it is made of electronic parts, then electronic failures apply. If

it is largely mechanical and dynamic (rotating, for example) then failures related to the bearings, shafts and seals also apply. To illustrate this, consider a large, motorized flow-control valve that contains many components. Tracking one of the essential components over time, like a bearing, provides good decision support for an appropriate lifecycle strategy. Figure 2 illustrates the condition profile of a bearing over time. The degradation of a bearing is often marked by an increase in torque.

In Figure 2, the declining mean time between failure (MTBF), marked by the shorter intervals, is as important as the level of performance achieved after each refurbishment. A declining performance after each restoration and decreasing service interval together may indicate that the asset is nearing the end of its useful life. It may be too expensive to maintain, or may be falling below minimum in-service performance requirements. The stress scoring, a reflection of the operating context and illustrated by the light blue line in Figure 2, offers clues to the decline.

The components that fail (bearings, in this case) and the rate at which they fail (days to weeks) greatly influence the strategy to employ. This is illustrated in the *P–F* part of the curve in Figure 2, and illustrates the point at which a failure potential is detected (*P*), and the point at which the asset or component has failed (*F*). See Nowlan and Heap for their discovery and discussion on this topic [1]. In con-
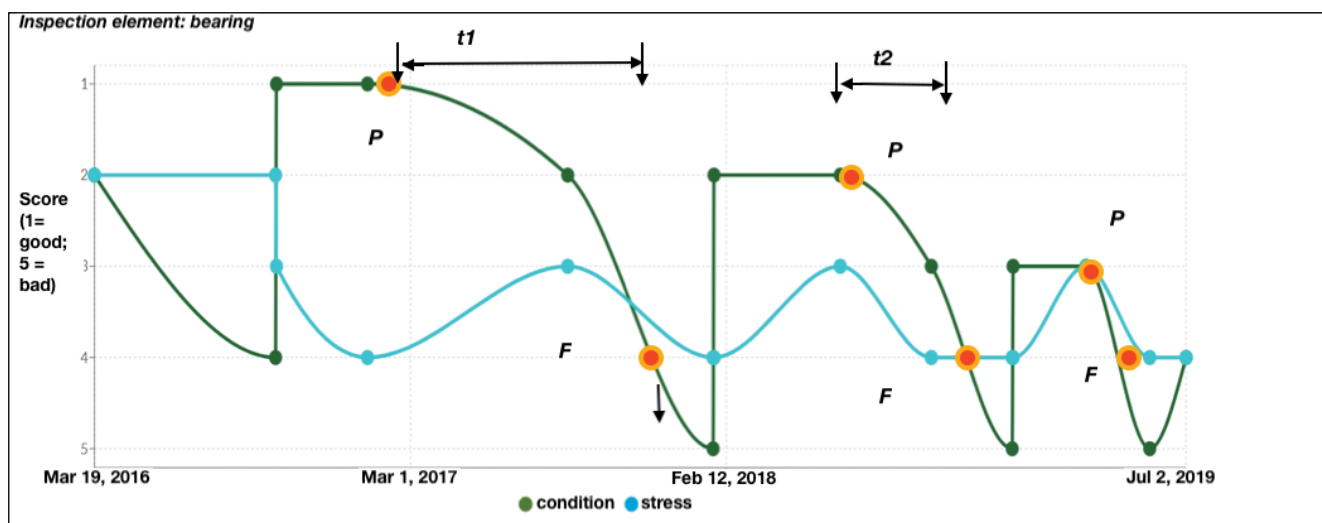

FIGURE 2. This chart shows the condition profile of a bearing over time. The bearing's degradation can be evaluated based on changes in the torque

trast to bearings, valve body coatings have a more linear failure curve and a far slower rate of failure, often on the order of years.

Inspections need to occur frequently enough to avoid missing the decline (P) once it starts. Assuming an inspection occurs prior to any noticeable degradation, the next inspection must occur at a point on the declining curve that leaves enough time to intervene prior to F, if failure is not an option. This would be the inspection at the end of time period t_1 in Figure 2.

The optimal inspection period will be determined over time and will be based on the valve asset characteristics and the local context. It may be adjusted over time given the changes in a component's failure-curve time period. This adjustment on shortened failure curves is illustrated in Figure 2 with t_2 is shorter than t_1.

Critical dynamic rotating assets, such as motorized control valves, pumps or compressors, should be inspected with sufficient frequency to be approximately one-half to one-third of the failure-curve interval to allow enough time to intervene, plan, mitigate and repair the asset without loss of service. This may not be possible with failure degradation curves on the order of days, in which case, any degradation in performance should trigger a work order.

Consider asset operating context

PM strategies will also be influenced by the service status of a valve using the following considerations:
• Lead versus installed bypass
• Rarely turned on or rotated
• Under high stress, such as exposure to waterhammer or cavitation, for example

The degree of usage versus its static state (no active use) influences how often an asset should be both inspected or require routine preventative maintenance. As an example, PM schedules should differ for assets in lead versus lag versus installed spare roles, with schedules ranging from aggressive monitoring and exercising to only occasional monitoring and exercising. Furthermore, installed spares versus the on-shelf spare would also likely have different PM schedules, the latter mostly involving corrosion prevention during storage. This is further modified by the stress the asset experiences, which may include:
• Frequent stopping and starting of motors, as opposed to occasional but continuous operation
• Temperature swings
• Environmental exposure
• General neglect
• Waterhammer

Identical assets experiencing significantly different levels of stress should have different inspection and PM schedules. Importantly, the specific stress will emphasize certain PM methodologies or type of monitoring to identify specific failures the asset

TABLE 2. EXAMPLE PM VALVE STRATEGY					
Failure mode	Rate of failure	Primary PM-driven strategy	Secondary PM- driven strategy (idle time)	Inspection frequency strategy	Base inspection type
Bearings	Months	Calendar	Event	Criticality-driven	Torque, vibration
Seals	Weeks	Calendar	Event	Criticality-driven	Leakage
Seats	Weeks	Calendar	Event	Criticality-driven	Leakage
Motor	Months	Event or Runtime	Calendar	Criticality-driven	Megger (insulation), Amps (motor load)
Shaft	Months	Calendar	Event	Criticality-driven	Visual, corrosion, torque, vibration
Electrical	Years	Calendar	Event	Criticality-driven	Visual, temperature, phase
Gasketing (if present)	Months	Event	Calendar	Criticality-driven	Efficiency
Coupling (if present)	Months	Calendar	Calendar	Criticality-driven	Visual, vibration
Ball/globe/knife/ butterfly vane/gate valves	Months to years	Runtime	Calendar	Criticality-driven	Leakage, vibration, visual, corrosion

manifests due to the load conditions.

Static valves, or valves never exercised, is a designated operating context that should be avoided when compared to a regularly exercised valve program. While exercising valves does introduce a failure mode of "wear" on mated parts and could potentially drive the valve to a failed state eventually, it does, however, provide a window into a valve's condition (even a declining condition), which is better than the alternative. A valve never exercised is an unknown quantity, and raises many questions for operations teams:
• Will the valve close if required or will it be seized?
• Will it seat properly if it does close most of the way?
• Is there corrosion or particulate matter buildup interfering with proper operation?

Similarly, any single-point-of-failure valves must be on a suitable condition-monitoring program to assure proper operation when required.

Cross-connection opportunities
Systems are a collection of assets grouped together to deliver on a primary function of that system — pumping liquid from location A to location B at a defined rate without leaking.

In some cases, a system may have a high redundancy of assets performing the same role, sometimes with substantial overcapacity, and may be sufficiently cross-connected via pipes and valves to offer significant increases in operational resilience. In other cases, a system may have very limited capacity to withstand upset

due to a single-service asset, a single-point-of-failure valve, or no cross-valving of the systems. When there are redundant assets, the cross-connection to backup assets can not only provide a high degree of assurance of service delivery, but will also reduce asset criticality compared to a single-asset configuration. As such, a less aggressive inspection cycle can be adopted, sometimes even to the point of permitting an asset to fail with little or no advance knowledge.
Example of network valve strategies. Table 2 gives a general guide for PM strategies for network valves. This set of strategies was developed with a client for their network valves following a comprehensive criticality and risk review, based on the equipment considerations below:
• Regular valve exercise program (all valves over 2 in. in diameter)
• Sleeve valves: regular monthly debris inspection and clear-out
• Shutoff valves greater than 12 in. in diameter: corrective action based on torque

Influence of runtime philosophy
PM strategies are also influenced by runtime philosophies, either favoring an unequal runtime mode of redundant assets or equal runtime mode of the same assets. The preferred operating mode will influence the asset management strategy. Equal runtime will generally warrant more monitoring of the valves and direct the choice of tools to catch detectable failure modes much earlier in the failure cycle. Equal runtime often results in all assets failing at around the same time, which more significantly

affects operations than a single asset outage. Considerations include the number of shelf spares and parts, the need for identical assets, large short-term rehabilitation costs to refurbish all at once at the annual turnaround versus the more discrete and smaller costs spread over the year for unequal runtime mode.

In summary
Asset strategies and PM strategies are influenced by and informed by several factors in an asset portfolio, including lifecycle stage, the criticality and risk rankings, asset condition, the valve's failure modes, overall process interconnectedness and redundancies, mandated level of service and operational philosophy. Each must be considered to appropriately manage the valves — not too much or too little, in the right way at the right time, and with the right discovery tools. ■
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Safely Operating a Heat-Transfer-Fluid System

Being aware of and understanding potential hazards are crucial for operating a heat-transfer-fluid system safely

A significant number of industrial processes require heating or cooling with precise temperature control. Maintaining this temperature control can be achieved through several industrial practices, but is most often done through a heat-transfer system. Such a system has many components, including, but not limited to, a pump, process adjacent-piping, valves, gaskets and a suitable heat-transfer fluid (HTF). HTF systems, depending on design and volume, may introduce several types of industrial hazards to a site. These hazards could be human-health based, such as thermal or inhalation exposures, or environmentally based, including accidental releases or unresolved fugitive emissions. However, any risk that an HTF system introduces can be mitigated with the correct system design, maintenance and operator training. As such, working with experts to design the system and using the correct HTF for your application, is a critical step in ensuring operator, environmental and public safety.

This article provides users with a resource that illustrates how to properly handle and maintain heat exchangers that contain HTFs with hazardous properties. Safe handling will be demonstrated through discussion on international and regional classification systems and their requirements, elucidation of hazard and risk, and how these requirements and issues relate back to proper system design and operator training.

To frame our understanding, it is worthwhile to briefly review the hazard classification systems applied in different regions. These classification systems are discussed in the boxes on p. 34 (international) and p. 36 (regional).

Hazard discussion

The use of HTF fluids with hazardous properties may imply certain risks for employees and the environment depending on the characteristics of the HTF. Besides the inherent risk derived from high temperatures and elevated pressures of the HTF system, the physical-chemical properties of some HTF products that allow sufficient thermal stability at high temperatures also result in additional hazards and, depending on the region, regulatory obligations for a site.

One hazard applicable to all HTFs used at high temperatures is the potential exposure of operators to high-temperature fluids or surfaces. A thermal exposure at process temperature may result in serious burns. Thankfully, there are ways to prevent thermal exposures, such as using adequate personal protection equipment, mechanical barriers and warning signs to prevent accidental contact with hot surfaces.

Other potential hazards found in using high-temperature HTFs may include aspiration, acute toxicity, reproductive toxicity and skin irritation or sensitization. In the following, we will use the definitions of the Globally Harmonized System of Classification and Labeling of Chemicals (GHS) [1]; they are also adopted in the European Regulation on Classification Labeling and Packaging (CLP) [2, 3].

Aspiration hazard. Hazard of acute effects caused by the entry of a liquid or solid chemical directly through the oral or nasal cavity, or indirectly from vomiting, into the trachea and lower respiratory system.

Acute toxicity. Adverse health effects occurring after a single or short-term oral, dermal or inhalation exposure to a substance or a mixture.

Reproductive toxicity. This refers to the adverse effects on sexual function and fertility in adult males and females, as well as developmental toxicity in the offspring, occurring after exposure to a substance or mixture.

Skin Irritant. A skin irritant is a substance that produces reversible damage to the skin occurring after exposure to a substance or mixture.

Skin sensitizer. A chemical that will lead to an allergic response following skin contact.

Acute aquatic toxicity. The intrinsic property of a substance to be injurious to an organism in a short-term aquatic exposure.

Chronic aquatic toxicity. This is the intrin-

Matthias Schopf and Joshua Baptist
Eastman Chemical Company
Dieter Drohmann
Chemservice Group

IN BRIEF

HAZARD DISCUSSION

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DETERMINING THE HAZARD AND RISK

SYSTEM DESIGN & MAINTENANCE

sic property of a substance to cause adverse effects to aquatic organisms during aquatic exposures, which are determined in relation to the lifecycle of the organism.

Aspiration hazards are a result of the low viscosity of fluids. Generally, if a chemical is ingested, instructions are to induce vomiting. However, low-viscosity fluids have a chance of aspiration, or entering the lungs, when vomiting is induced. If operators are aware of what to do when an ingestion exposure occurs, there is little to no risk for this hazard.

The remaining human health and environmental hazards are a result of the physical-chemical properties that are necessary for HTFs to offer the thermal stability necessary for process heat integrity. HTFs must be persistent in environments of high pressure, temperature, flow and, in some systems, with contaminants. As such, persistence, bioaccumulation and toxicity (PBT) listings, reproductive toxicity, and aquatic acute and chronic ratings tend to be prevalent in the highest temperature chemistries.

Finally, operators must consider physical hazards that HTFs present. GHS describes 17 physical hazards, but HTFs should mainly consider the flash point, flammability and boiling point. A substance is considered as a flammable liquid if it has a flash point of not more than 93°C. While fluids with higher flash points are not subject to classification, they may also be a potential safety hazard when operated above the flash point. This is usually the case for many HTF systems, because most industrial processes require operating temperatures well above the flash point of HTFs. This is why it is important for operators to have designed a system that minimizes leaks of fluid or vapors. When fugitive emissions occur, this is the event that is most likely to result in significant issues for system operators. There is a risk that hot vapors or liquid in insulating material ignites with the right conditions (temperature, humidity, physical state of emission). Therefore, if you have any concerns about your system, please consult with an expert to ensure system integrity.

Legally mandated information on all potential hazards for a substance will be published in the safety data sheet

INTERNATIONAL HAZARD-CLASSIFICATION SYSTEMS

The Globally Harmonized System of Classification and Labeling of Chemicals (GHS) is the internationally accepted standard and was introduced by the United Nations (UN). Regarding classification and labeling, GHS is majorly adapted or represented in nearly every chemical legislation globally. This mandate to develop and establish a classification system was ratified by the UN Conference on Environment and Development (UNCED) in 1992. In chapter 19, from the agenda of UNCED, the following was concluded: *"A substantial use of chemicals is essential to meet the social and economic goals of the world community, and today's best practice demonstrates that they can be used widely in a cost-effective manner and with a high degree of safety"* [4]. However, UNCED also concluded that there was a lack of information and resources for the risk assessment of chemicals. In response, governments have been expanding and accelerating programs for the assessment of chemicals, harmonization on classification and labeling, and information exchange on chemical risks.

The first edition of GHS was published in 2003 and has been subsequently updated about every two years. The ninth revision was published in September 2021. This revision was also joined with a compiled list from the GHS subcommittee secretariat of the 85 countries that have implemented and adapted the GHS requirements [5]. This wide implementation illustrates how GHS has become a truly global system for classification and labeling. Most recently, the tenth revision has been published with some additions about classification procedure for desensitized explosives and the use of non-animal testing methods for classification of health hazards.

In practice, the primary functioning of the GHS system is to provide classification and labeling criteria for responsible parties. To do this, GHS differentiates between physical, human and environmental hazards. There are several sub-categories of these hazards, including physical-chemical property descriptors, like flash point and boiling point, as well as human health descriptors, including reproductive toxicity, skin irritation and aspiration toxicity. These hazards and their descriptors are established via testing parameters standardized by GHS. In most regions, the onus for generating test data for new or existing products is placed upon manufacturers. When data are generated, the behind-the-scenes process includes a manufacturer that has commissioned a laboratory that follows the outlined GHS standards to produce that data or has otherwise internally produced standard-compliant results themselves. The responsible company must then classify and label that product according to the laboratory results and the requirements outlined in GHS. Each of the 85 countries and regions that have adopted the GHS guidelines have also adapted their own approaches to this system that are either just as strict, or stricter, than the GHS system. ❑

(SDS) of the product and are summarized as well on the product label. In addition to the hazard identification, this document will also provide information about the supplier and emergency responses, first-aid measures, accident prevention, measures for safe handling and storage, transport provisions, and international and country-specific national regulations. In Europe's REACH legislation, the SDS must include an annex that provides users with exposure scenarios. SDSs generally cover everything that a user of the material will need to know. Facilities should continuously review their hazardous material SDSs, handling procedures, local and national requirements, and the publicly available data to ensure they are providing the safest possible environment for operators.

Determining the hazard and risk
When facilities design their heat-transfer systems, they should incorporate considerations for haz-ard and risk relating to operators and the environment. A hazard is a scenario where an adverse event can occur, and the risk is the likelihood of that adverse event occurring. For example, not remediating fugitive emissions may result in a fire hazard around the emission area. It should be noted that fugitive emission volume tends to be low, it must encounter another flammable material, and the emission would need an appropriate ignition source. With these considerations in mind, a hazard is very obviously present, but the risk may be somewhat limited. This is to say that a fugitive emission will always present a hazard with varied risk due to environmental and system conditions. Therefore, this type of risk is widely understood to be unacceptable for the operator, facility and environment, and it should be remediated accordingly. During that remediation, additional examples of hazard and risk are demonstrated. Generally, it is

recommended that operators purge the HTF system with nitrogen and lower the system's temperature to less than 100°C before opening. Performing these steps removes the most significant hazard altogether by removing hot volatile organics as a possible exposure. If these steps are not tenable for one reason or the other, operators can be provided with proper ventilation in the environment if the system is indoors, personal protective equipment and training to perform tasks quickly and effectively.

The key for minimizing both exposure and emissions is to operate the HTF in a strictly controlled closed system. When the heat-transfer system is operated in this manner, the risk of fluid release and any potential exposures are minimized. Maintenance and routine events, filling and draining, are the major points of exposure for operators. A few of the additional routine tasks that should have developed procedures and safety considerations are outlined below:

• Maintaining or exchanging equipment on the process side of heat exchangers
• Cleaning pump strainer and/or the side-stream filter
• Replacing the sealing of a pump
• Exchanging a defective instrument or valve on the HTF loop
• Replacement of gaskets on flanges
• Cleaning or removal of fluid from equipment, such as the expansion vessel that needs to be inspected by manual entry and HTF sampling for routine analysis

The best way to minimize exposure risk is to ensure your system is properly designed. The procedures for that system should be standardized and captured in formal documentation. Also, personal protective equipment (PPE) and proper training should be provided for operators of the system. All of these safety considerations should align with your facility's regional and national requirements. PPE is the last line of defense against exposures for operators. Facilities should consider all other aspects of the hierarchy of controls as they develop their system design. By the end, facilities should have a closed system that only presents hazards to operators when opened hot. As such, facilities can employ procedural, administrative and PPE controls to further minimize any risk of exposure. Suggested PPE for an HTF system includes gloves, long sleeves, goggles and chemical-resistant footwear. It is also recommended that operators don additional protection for the eyes and skin using chemically resistant aprons and face shields.

System design & maintenance

"*Applying appropriate constructive and design measures, in combination with organizational measures, can also lead to permanently technically tight plant(s). Apart from the human and technological factors, the organizational structure for safety measures also plays a key role when it comes to plant safety*" [8].

Heat-transfer systems, when designed and maintained properly, are low-cost, low-exposure and low-maintenance systems to have on an industrial site. Scheduling of maintenance events can vary from user to user, but it is generally recommended that systems are sampled every 12 months and that system inspections occur according to technical and regulatory requirements. System inspections may result in the need to perform system maintenance. Primary outcomes of system inspections, and the resulting maintenance activities, are highlighted below.

For the maintenance scenarios, operators should always consider their own procedures first. Operators should also be cognizant of requirements laid out by their national and regional authorities when developing or adapting procedures.

Filling and draining. Prior to unloading the contents of a bulk container, it should be properly positioned for safe access, centered in front of an unloading dock, and within spill containment areas. If bulk-container heating is required during unloading, which is typically performed with pressurized steam, it is important not to exceed the maximum allowable pressure rating of the bulk container. The maximum allowable pressure of the bulk container can vary and should be referenced before unloading. HTF systems are normally filled from the bottom to the top. This technique is employed to prevent aeration of the fluid. While filling, top vent(s) on the system should be opened for displacement of the vapors from the system to a predetermined and predictable location. During the filling process, it is recommended to have person-

REGIONAL HAZARD-CLASSIFICATION SYSTEMS

One example of a region's adoption and expansion of the GHS system can be seen in the European Regulation on Classification, Labelling, and Packaging (CLP). The European regulatory framework adopts most of the GHS guidelines as is, but it does have some important distinctions.

GHS guidelines for some human and environmental health hazards have cutoffs of 0.3%, but the CLP lowers those concentrations to less than 0.1%.

Harmonization of classifications can be initiated by the European Chemical Agency (ECHA) or E.U. Member States when data from studies provide a justification to do so. This can be a response from classifications and labels that are required to be submitted for substances on the E.U. market in the C&L inventory.

The E.U. has an adjoining poison control harmonization scheme where substances in classified mixtures are assigned UFI numbers that downstream users can reference when calling the Poison Center Notification (PCN) hotline with an exposure event. This system is protective of confidential business information (CBI) and protects downstream users when exposures occur.

Another important regulation related to, but independent of CLP, is REACH (Registration, Evaluation, Authorization and Restriction of Chemicals). The ECHA describes REACH as *"… a regulation … adopted to improve the protection of human health and the environment from the risks that can be posed by chemicals"* [6]. In practice, REACH's primary function is to register, evaluate, authorize and restrict or ban substances that are placed on the European market. REACH came into force in 2007, with pre-registration phases and transitional periods that ended in 2018. Following the end of the transitional period, REACH is now fully implemented and applies to all Member States of the E.U. and three additional countries (Iceland, Liechtenstein and Norway), which constitute the European Economic Area. REACH provides valuable resources to individuals and corporations alike by summarizing data into REACH dossiers. These dossiers contain information from the identity of the substance to safe handling and toxicological properties. It is recommended that users familiarize themselves with the ECHA registered substance database to ensure they understand all the hazards associated with a substance.

Another important facet of regional regulatory framework implications is additional classifications that are not GHS based. REACH adds additional hazard characterization through listing systems, such as the Persistent, Bioaccumulative and Toxic (PBT) and Substances of Very High Concern (SVHC) listings. These listings are described in detail by the REACH legislation, but the key takeaway is to understand that the E.U. has additional tools that can heighten and accelerate the regulatory scrutiny of certain chemistries. This means that these chemistries may see accelerated paths towards regulatory measures on the European market.

In addition to the international regulations, additional requirements can be laid out by the national authorities.

Some examples

Germany follows the requirements laid out in the Seveso III Directive, but it also employs its own water hazard classification under Ordinance on facilities for handling substances that are hazardous to water. Switzerland has a special regulation to reduce emissions of volatile organic compounds (VOCs), while France introduced an extended producer responsibility that requires producers to contribute to the disposal of waste from their products. In the U.S., the Environmental Protection Agency (EPA) has proposed rules for notifying about the use of certain chemicals in significant new uses (SNUR) under the Toxic Substances Control Act.

All these regulations have important implications for operators of HTF systems. Lowered concentration limits, classification harmonization procedures and all the different listings can introduce administrative and financial burden on industrial sites. As such, it is important for downstream users to stay up to date with these listings and be familiar with the regulatory inventory databases, such as the ECHA database [7]. ☐

Therefore, non-combustible absorbent material (either pads or bags filled with granular solids) that soaks up spilled HTF should be readily available.

Periodic inspections. Good examples for inspection checklists can be found in Ref. 8 and 9.

Industry standards and practices have been established and developed regarding design, construction and operation of a closed HTF system [*8–19*]. They are published by industry associations, industry standard bodies, insurance companies and regulatory authorities. These standards can vary from region to region, but there are some common principles to keep in mind when designing your system to minimize the risk of release and exposure. These include the following.

Location. The heat-transfer system should be located on an impermeable surface to avoid soil contamination. This area should be designed to allow containment of any leakage and to ease any cleanup efforts. To achieve this, it is recommended to slope the areas under equipment, use dikes and other controlled drainage to divert leakage and runoff to a safe location [*9*]. Considering the equipment, all components selected need to be designed to withstand the desired operating temperatures and pressures. This design must include a satisfactory safety margin which can be referenced from industry experts or within technical guidance documentation within your region. Reference and understanding of the required codes and regulations, as well as the equipment manufacturers' design data sheets is essential for a proper fluid selection.

Piping. Pipework and pumps are given extra attention within the standards due to their higher likelihood of fluid or vapor release. Pipework flanges should be minimized and welded as much as is technically and economically feasible. For easier inspection and maintenance, flanges should be located where they can be regularly inspected. In higher temperature heat-transfer systems (>250°C), flange connections made of stainless-steel spiral-wound gaskets with a flexible graphite insert have been proven to be reliable. Where these materials aren't available

nel inspecting the piping network to confirm there are no leaks.

Maintenance and repairs. Any maintenance and repair task must be carefully planned to reduce the risk of fluid release. Some typical maintenance activities, like pump seal repair, are performed in areas where fluid containment infrastructure is already implemented. Despite this, it is recommended that a review of potential leakages regarding location and volume should be performed prior to each maintenance event.

Sampling. When performing in-service fluid sampling, besides standard PPE, operators may also consider VOC filtering respirators. An even better management of system sampling is to use an in-line sampler, which removes the potential of exposure from the operator.

Spills. For all operations it is important to clean up any spill immediately.

or economically feasible, pure graphite gaskets have proven to be a reliable alternative. Proper installation is critical, as gaskets are only used once. Threaded connections should be eliminated from use within an HTF system, because they are difficult to seal. As a final note, it is important to do a proper stress analysis of the pipework and provide sufficient room for thermal expansion and contraction by deploying stress-relief components throughout the system. Stress-relief components can include hangers, expansion joints and expansion loops.

Pumps. Three different pump types are utilized in HTF systems: centrifugal, canned motor and magnetic driven. All three types of pumps are valid choices for a heat-transfer system. However, it is worth noting that choosing a centrifugal pump will require that the pump come equipped with a double mechanical seal or a liquid barrier, or both, to minimize any potential of leakage from the pump. To ensure a long life for the pump, with minimal emissions, the alignment of the pump and motor should be done while the pump is hot. Special attention should be given to minimizing the risk of thermal burns while doing this alignment. So, it is important to consider exposure potential and regional and national requirements on protection when performing this maintenance step. Pump leaks from the shaft seal must be safely diverted and collected [13].

Besides the hardware, another important factor to minimize the risk in operating an HTF system is to employ proper procedures and adequate training. The U.S. National Fire Prevention Association (NFPA) has stated "most cases of failures can be traced to human error. The most significant failures include inadequate training of operators, lack of proper maintenance and improper application of equipment" [10]. Therefore, all employees working with HTFs must be trained in established handling procedures and specific instructions of how to operate the system. The importance of this is highlighted by the fact that more than 50% of claims related to incidents with thermal fluid systems are neither equipment nor design re-

lated [14]. A thorough inspection and detailed training plan needs to be developed to ensure high plant reliability and safety is in place to minimize the risk of chemical exposure.

Any risk stemming from the hazardous properties of HTFs can be managed. The risk associated with the different hazards of HTFs are controlled by minimizing the release and exposure of chemicals through system design and proper training. The biggest health risk associated with a heat transfer system is the risk of thermal burns. This risk can be effectively reduced by correct design and handling. Heat transfer systems of all process temperatures and fluids can be operated in a safe manner, for employees and the environment. ∎

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Solids Flow Measurement in Specialty Chemicals: Seamless Integration

Continuous flow measurement is used at this Austrian specialty chemicals manufacturer for process optimization, as well as overload protection

Christoph Hillebrand
Siemens

Sensing-plate weighing systems are often used for weighing free-flowing and very dusty bulk materials. Such solids flowmeters ensure reliable determination of material throughput rates, even in harsh environments. An Austrian specialty chemicals manufacturer uses continuous-flow measurement for process optimization of its additive production, as well as for overload protection of separating sieves — over a wide measurement range.

Background

Additives are auxiliary substances or supplements and contribute significantly to improving the properties of the main product, either during production, storage and processing or in subsequent application. For most additives, the rule is: minimum use, maximum effect. They are always optimized for special applications, and are often custom-made. This results in rather low production volumes and a very high effort in research and development.

Tribotecc GmbH (Arnoldstein, Austria; www.tribotecc.com), a member of the Treibacher Group, is the world's leading manufacturer of metal sulfides. As functional additives, metal sulfides are used in brake and clutch linings, as well as in lubricants and abrasives. More than a dozen natural and special synthetic metal sulfides are available. At the specialty chemicals company, therefore, everything revolves around friction. The science of friction (tribology) explores the relationships between friction, wear and lubrication.

These relationships are of immense importance for our everyday lives, as well as for the economy — they determine the wear of machines, as well as energy consumption and thus CO_2 emissions. Around the world, Tribotecc's innovative products help ensure, for example, that engines consume less, gearboxes last longer or bearings are practically maintenance-free due to synthetic solid lubricants.

Key to quality

Consistent product quality is crucial to the success of the company. The manufacture of the precisely specified products is subject to permanent quality checks.

The exact dosing of the individual ingredients has been carried out with Siwarex load cells from Siemens for more than ten years. A total of more than two dozen weighing stations, some of which are calibratable, are equipped with Siemens technology and integrated into the control system via Simatic I/O systems and controllers. "We

FIGURE 2. One of three bulk flowmeters of the Sitrans WF330 series is shown here. The weighing mechanism is externally mounted, which protects the flowmeters from dust, corrosion and wear

have been very satisfied with the technology we have been using for years," explains Markus Franzel, who is the responsible manager for EMSR (electrical, instrumentation and control) plant engineering at Tribotecc. "My team and I take care of the integration and modification of the Siemens weighing technology ourselves here in Arnoldstein."

To this end, Franzel and colleagues visited Siemens' Weighing Technology Center in Karlsruhe, Germany. Here, not only are Siwarex application possibilities shown in action, but customer-specific training courses are also held. "With the knowledge we gained, we were optimally equipped for the automation of our batching and weighing tasks," Franzel recounts. "And if there are ever any unanswered questions," he continues, "Siwarex Support is there to help us. Here, we always get competent answers at short notice from weighing specialists who know our application."

New sieving technology

In the processing of a natural metal sulfide, an existing aggregate used to separate constituents was to be replaced by two sieving steps. "With

FIGURE 1. This diagram illustrates the operating principle of a bulk flowmeter. The impact force of the material deflects the baffle plate, and the processing electronics record the horizontal component of the reaction force. This signal is converted into a throughput quantity

Siemens

FIGURE 3. For continuous monitoring, one of the screens is supervised by WF330 bulk flowmeters for filling and filter rupture

the sieve or to be able to check it for mechanical damage," explains Franzel, the principle.

Benefits

The solids flowmeters were to cover three application ranges: up to 2,600 kg/h, up to 1,200 kg/h and up to 450 kg/h. "The committed accuracy of ±1% is crucial for our processes. The fact that we can now cover such a wide measuring range with the Siemens solids flowmeters and always precisely determine the throughput of the powder makes a significant contribution to maintaining our specified product quality," says Franzel.

The load cells are connected via the Siwarex FTC (Flexible Technology for Continuous Weighing) function module. It can be clipped onto the backplane bus of Simatic ET 200 I/O systems with minimal cabling effort. The weighing module calculates and totals the flowrate and can be controlled via the existing Simatic S7-300 automation systems. "We did the integration via Siwatool," reports the EMSR manager, adding

with amusement, "It was smooth or — as we like to say at Tribotecc — absolutely frictionless." The service software can be used to parameterize and adjust Siemens weighing systems, read out diagnostic messages and conveniently save or upload configuration files.

Tribotecc is very satisfied with the application of the three solids flowmeters, which now complement the extensive portfolio of Siemens weighing systems: "We achieve optimum throughputs in all application areas, our product quality benefits from precise weight measurement and we have monitoring of our sieves at the same time," summarizes Franzel. ■

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this measure, we wanted to further improve product quality and operating principle of a bulk flowmeter: The impact force of the material deflects the baffle plate accordingly [Figure 1]. The processing electronics record the horizontal component of the reaction force and this signal is converted into a throughput quantity," explains the manager for control technology and the modification. "However, the material feed is very tricky, because if it is overloaded, the sieve gets cracks and then the product quality is no longer guaranteed. In the worst case, the batch is lost."

The EMSR team solved this task with the help of three Sitrans WF300 series solids flowmeters from Siemens (Figure 2). For the flow measurement and the avoidance of sieve overloads, one solids flowmeter is responsible at Tribotecc. A second one is used for quality control. It is installed behind the sieve unit (Figure 3), so that a sieve rupture can be identified by detecting unexpected flowrates. "We have programmed the system in such a way that, in the event of a trend deviation, the dosing is automatically reduced in order to relieve

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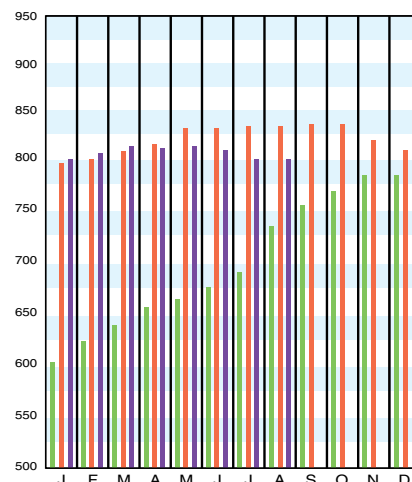## FOR ADDITIONAL NEWS AS IT DEVELOPS, PLEASE VISIT WWW.CHEMENGONLINE.COM

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CHEMICAL ENGINEERING PLANT COST INDEX (CEPCI)

(1957–59 = 100)	Aug. '23 Prelim.	Jul. '23 Final	Aug. '22 Final
CE Index	798.7	798.7	824.5
Equipment	1,004.1	1,005.5	1,046.7
Heat exchangers & tanks	822.2	822.6	879.5
Process machinery	1,026.8	1,026.6	1,054.5
Pipe, valves & fittings	1,338.9	1,348.0	1,480.9
Process instruments	562.4	562.1	556.8
Pumps & compressors	1,501.7	1,501.7	1,305.3
Electrical equipment	801.7	800.0	775.3
Structural supports & misc.	1,129.2	1,129.3	1,185.0
Construction labor	372.8	368.5	358.9
Buildings	812.6	810.7	825.8
Engineering & supervision	313.0	313.1	311.6

Annual Index:

2015 = 556.8
2016 = 541.7
2017 = 567.5
2018 = 603.1
2019 = 607.5
2020 = 596.2
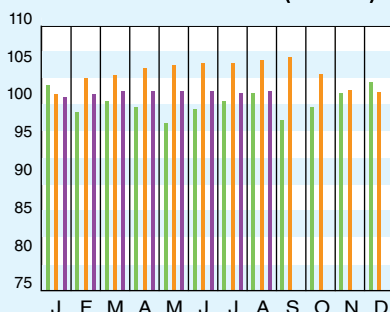2021 = 708.8
2022 = 816.0

Starting in April 2007, several data series for labor and compressors were converted to accommodate series IDs discontinued by the U.S. Bureau of Labor Statistics (BLS). Starting in March 2018, the data series for chemical industry special machinery was replaced because the series was discontinued by BLS (see *Chem. Eng.*, April 2018, p. 76–77.)

CURRENT BUSINESS INDICATORS

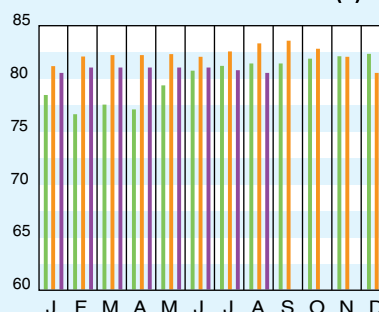|	LATEST		PREVIOUS				YEAR AGO	
CPI output index (2017 = 100)	Aug. '23 = 99.4		Jul. '23 = 99.0		Jun. '23 = 99.4		Aug. '22 = 100.7	
CPI value of output, $ billions	Jul. '23 = 2,359.0		Jun. '23 = 2,323.9		May '23 = 2,311.0		Jul. '22 = 2,516.0	
CPI operating rate, %	Aug. '23 = 79.1		Jul. '23 = 78.9		Jun. '23 = 79.2		Aug. '22 = 81.1	
Producer prices, industrial chemicals (1982 = 100)	Aug. '23 = 304.1		Jul. '23 = 310.1		Jun. '23 = 319.7		Aug. '22 = 358.1	
Industrial Production in Manufacturing (2017 =100)*	Aug. '23 = 99.7		Jul. '23 = 99.6		Jun. '23 = 99.2		Aug. '22 = 100.4	
Hourly earnings index, chemical & allied products (1992 = 100)	Jul. '23 = 225.4		Jun. '23 = 222.6		May '23 = 219.0		Jul. '22 = 202.8	
Productivity index, chemicals & allied products (1992 = 100)	Aug. '23 = 90.8		Jul. '23 = 91.9		Jun. '23 = 91.5		Aug. '22 = 91.2	

CPI OUTPUT INDEX (2017 = 100)†

CPI OUTPUT VALUE ($ BILLIONS)

CPI OPERATING RATE (%)

*Due to discontinuance, the Index of Industrial Activity has been replaced by the Industrial Production in Manufacturing index from the U.S. Federal Reserve Board.
†For the current month's CPI output index values, the base year was changed from 2012 to 2017
Current business indicators provided by Global Insight, Inc., Lexington, Mass.

CURRENT TRENDS

The preliminary value for the *CE* Plant Cost Index (CEPCI; top) for August 2023 (most recent available) is unchanged from the previous month, although some of the subindices making up the composite index did show offsetting increases and decreases. In August, the Equipment and Engineering & Supervision subindices fell by small margins, while the Buildings and Construction Labor subindices each rose by small amounts. The current CEPCI value now sits at 3.1% lower than the corresponding value from August 2022. Meanwhile, the Current Business Indicators (middle) show increases in the CPI Output Index and the CPI Operating Rate for August 2023, and an increase in the CPI Value of Output Index for July 2023.